Effect of thermal stabilizers on the photo-oxidative degradation of solid poly(vinyl chloride)

T. A. Skowronski*, J. F. Rabek and B. Rånby
Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden
**Institute of Organic and Polymer Technology, Technical University, Wroclaw, Poland*

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It has been found that metal (Ba, Ca, Cd and Pb) stearates and pure stearic acid have stabilizing effects on the photodehydrochlorination of poly(vinyl chloride) (PVC) and the formation of polyene structures. On the other hand the same compounds accelerate photo-oxidation of PVC. From oxygen uptake measurements at different temperatures we calculated the energy of activation of photo-oxidation. It was found that metal stearates decrease the energy of activation of photo-oxidation processes of PVC, whereas stearic acid increases it. A synergistic effect of an equimolecular mixture of Ba and Cd stearates has also been observed.

Keywords Thermal stabilizers; metal stearates; photo-oxidative degradation; poly(vinyl chloride); polyene structures

INTRODUCTION

Processing of poly(vinyl chloride) (PVC) which takes place within the temperature range 160°–200°C requires addition of thermal stabilizers to decrease thermal degradation of the polymer[1-4]. The rate of thermal degradation can be reduced to a level which is acceptable from a technological point of view. Addition of stabilizers to the polymer may, however, have an unexpected effect on its photostability. The photochemical instability of PVC severely limits the potentially large outdoor applications of the polymer[5-10].

A large number of substances and mixtures have been suggested for the thermal and/or photochemical stabilization of PVC, which is generally supplied unstabilized by the manufacturer. The stabilizing systems vary according to the starting material, the processing and the field of application. Synergistic effects are often observed when different stabilizers are combined, i.e. the stabilizing action of the mixture is better than one would expect from summation of the individual effects.

The effect of thermal stabilizers on the thermal degradation of PVC was the subject of several publications. The most widely investigated group of thermal stabilizers are metal stearates[11-22]. The present knowledge of the effect of thermal stabilizers in PVC mixtures indicates that, in addition to their function of binding hydrogen chloride, the stabilizers can replace labile chlorine atoms in the chain, change polyene sequences, reduce colour of the degrading polymer and reduce the effects of compounds which catalyse dehydrochlorination.

In our previous studies we have found that organo-tin stabilizers of the type R_2SnY_2 (e.g. Advastab TM-181S, Irgastab 17M, Thermolite 25 and others) may enhance crosslinking of PVC[23]. Under u.v. irradiation these thermostabilizers are easily decomposed into different types of free radicals which may react further with double bonds present in partially dehydrochlorinated PVC and cause crosslinking.

Owing to limited information concerning the effects of added metal stearates (only calcium stearate) on the photostability of PVC[24,25], we have decided to investigate this problem much more broadly and the results obtained are presented in this paper. These results should be useful for producers and consumers of PVC. However, they were made with much shorter (254 nm) light than that found in sunlight (>285 nm).

EXPERIMENTAL

Suspension-polymerized PVC (Pevikon S-598) was obtained from Kema-Nord AB, Sweden, in the form of a white powder. The manufacturer's data are: Fikentscher K-value 59, $\bar{M}_n = 45000$, $\bar{M}_w = 102000$, i.e. polydispersity factor 2.27.

The following four metal stearates were investigated:

(1) Ba stearate (supplied by Swedstab AB, Perstop, Sweden),

(2) Ca stearate (Listab Ca) (supplied by Metallgesellschaft, Germany),

(3) Cd stearate (Cd16 S1-AY) (supplied by Börlocher, Germany),

(4) Pb stearate (Listab 28) (supplied by Metallgesellschaft, Germany), along with

(5) stearic acid (supplied by Metallgesellschaft, Germany).

The composition of the PVC compounds was as follows: to 100 g PVC was added 2.5×10^{-3} M or 5.0×10^{-3} M of the various stearates or a combination for

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the study of synergistic effects. All compounds were homogenized for 5 min on a laboratory two-roll mill at 160°–165°C. Rolled foils (skin) 0.8 mm thick were further pressed at 200 kg cm^{-2} at 175°C for 3 min to the thickness 50–100 μm. 'Pure PVC' samples were prepared under the same conditions without added stearates.

U.v. absorption spectra were recorded using a Perkin–Elmer 575 u.v./visible spectrometer, and i.r. spectra using a computerized Perkin–Elmer 580 B spectrometer.

Dehydrochlorination was measured by a conductimetric method described elsewhere[26–28]. The reaction photocell was made from quartz through which air, with CO_2 removed by using an ascarite column under normal pressure (1 atm), was passed. Air was used both as oxygenation gas and as carrier gas. The hydrogen chloride evolved during u.v. irradiation of PVC (0.3 g of an area 30 x 30 mm) was carried away from the photocell by air to a conductometric cell. The evolved hydrogen chloride was completely absorbed in a conductivity measuring cell, containing 30 ml of doubly distilled water. The electrical conductivity of the solution was measured by electrodes (type EA 608-01, Mehtrom Herisau, Switzerland) with the constant $c = 0.0785\ \mathrm{cm}^{-1}$ connected to a conductometer (type E 518, Methrom Herisau, Switzerland) with automatic correction for temperature variations. Concentrations of hydrogen chloride of about 10^{-7} M could be measured, which correspond to evolution of about 10^{-4}% of HCl when a 0.3 g sample of PVC was used.

The oxygen uptake was measured by a specially constructed oxygen pressure monitor with a pressure transducer (Vallidyne type P 10) mounted into a metal cell with a quartz window which was immersed in a thermostated water bath at 20°–60°C ± 0.01°C. PVC film samples of 2 cm diameter were first pre-evacuated at 10^{-5} torr and the cell was filled with pure oxygen at 1 atm. The oxygen uptake was monitored with a CD 12 transducer and *XY* recorder. The amount of hydrogen chloride evolved during u.v. irradiation of PVC samples does not have a visible effect on the kinetics of oxygen uptake in the performed oxygen uptake measurements.

The gel content of the PVC samples was measured by extracting 0.5 g (W_1) with THF for 24 h in a Soxhlet apparatus equipped with coarse Alundum thimbles (RA 98) which retain particles larger than 20 μm. The weight of the insoluble portion (W_2) was measured after drying to constant weight. The gel content (in wt%) was calculated as $100(W_2/W_1)$.

The following light sources were used for u.v./visible irradiation of PVC samples:

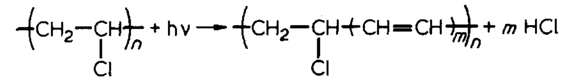
(1) High-pressure Hg lamp (type SP 500 W, PF 318 E, from Philips, Holland): u.v. spectra, dehydrochlorination rate and oxygen uptake at different temperatures were measured.

(2) Low-pressure Hg lamp (type RUL 120 W, eight lamps in a Rayonet photoreactor, type Merry-go-Round RPR-208, from The Southern New England Ultraviolet Company, USA): i.r. spectra and gel formation kinetics were measured.

Both lamps produce mainly u.v. radiation at 254 nm. The choice of these lamps was dictated by the short irradiation time of the samples possible. Using 'sunlamps' which produce light with wavelengths >285 nm requires very long irradiation times up to 2000 h or more. Experiments performed over such long times give much more scattered and less reproducible results.

RESULTS AND DISCUSSION

The primary products which are formed during heating and/or u.v. irradiation of PVC are hydrogen chloride (HCl) and conjugated polyene sequences:



$$\left(\mathrm{CH_2{-}\underset{\underset{Cl}{|}}{C}H}\right)_n + h\nu \longrightarrow \left(\mathrm{CH_2{-}\underset{\underset{Cl}{|}}{C}H}\left(\mathrm{CH{=}CH}\right)_m\right)_n + m\,\mathrm{HCl} \qquad (1)$$

All accompanying processes such as chain degradation, crosslinking, and formation of polyene sequences of various length and length distribution are influenced by the primary reaction (1) in which HCl is formed[10,29–36]. The effect of HCl on the photolysis of PVC is additionally complicated by the formation of a thin surface layer of highly light-absorbing polyene groups as chromophores[37,38]. These groups can be excited by absorption of light and may further participate in energy transfer processes, e.g. decomposition of hydroperoxide groups. It has also been concluded that the initial autocatalytic effect of HCl is due to an acid-catalysed decomposition of peroxy radicals forming carbonyl groups and hydroxyl radicals[38]. On the other hand HCl can be photochemically added to polyenes in the solid state[39].

Formation of polyene structures can easily be monitored in u.v. irradiated PVC by u.v./visible spectroscopy (*Figure 1*). Absorption in the region 270–450 nm is attributed[40,41] to the formation of polyene structures $-(\mathrm{CH{=}CH})_n-$, where $n = 3$–15. Individual polyene structures have overlapping absorption. As an example, trienes have three main maxima and higher polyenes usually have four. The extinction coefficient of a polyene is a linear function of the number *n* of conjugated bonds in the given sequence[40,42]. The effect of an increase of conjugated double bonds *n* is a displacement of the spectrum to longer wavelength. In u.v.-degraded PVC there are several sequences of conjugated double bonds ($n = 3, 4, 5$, etc.) which give composite u.v. spectra (*Figure 1*). The increased absorption at 280 nm is attributed to the formation of the shortest polyene sequence with $n = 3$. The decrease in absorbance at longer wavelength with a corresponding increase at shorter wavelength (at 280 nm) may be attributed to the reaction of polyene sequences $(\mathrm{CH{=}CH})_n$ with HCl with the formation of shorter sequences having an absorption at shorter wavelength. The fact that the rate of reaction depends on the HCl pressure and appears to reach a limiting value (50% of its initial intensity for 1 atm) suggests that the process is reversible and may occur in two ways:

$$(\mathrm{CH{=}CH})_n + \mathrm{HCl} \xrightleftharpoons{+h\nu} (\mathrm{CH{=}CH})_{n-1}\mathrm{CH_2{-}CHCl}- \qquad (2)$$

or

$$(\mathrm{CH{=}CH})_n + \mathrm{HCl} \xrightleftharpoons{+h\nu} (\mathrm{CH{=}CH})_x{-}\mathrm{CH_2{-}CHCl}(\mathrm{CH{=}CH})_{n-x-1} \qquad (3)$$

depending on whether the addition of HCl takes place inside or at the end of a polyene sequence[10,39,43,44].

The increased absorption at 280 nm occurs both in an oxygen-free atmosphere and in the presence of oxygen.

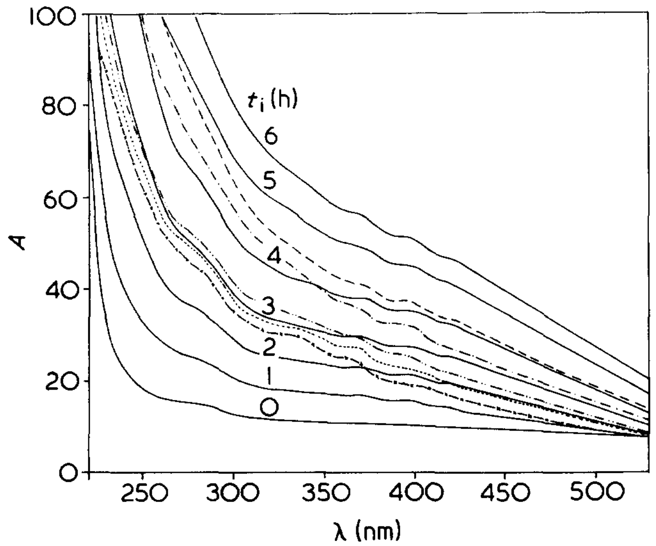


Figure 1 U.v./visible absorption spectra of polyene structures formed during u.v. irradiation (1–6 h) of PVC film in air (solid lines) and PVC film containing 2.5×10^{-3} M metal stearates or stearic acid per 100 g of PVC (broken lines): –×–, Ba+Cd stearates; - - - -, Ba stearate; –··–, Cd stearate; –·–, Ca stearate; ———, steric acid after 6 h u.v. irradiation

Oxygen itself has no strong effect on the polyenes formed in solid PVC during u.v. irradiation. The propagating polyenyl radical $-\!(CH=CH{-}\dot{C}H{-}CHCl)\!-$ is short-lived. It may split a Cl radical and grow one -ene unit. It may also add molecular oxygen and form a peroxy radical. In PVC polymer matrix, the reaction with oxygen is diffusion controlled and therefore slower than the Cl radical splitting.

The increased absorption at 280 nm can also be partially attributed to the formation of carbonyl (CO) groups which have an absorption maximum at the wavelength 280 nm. During short times of u.v. irradiation (1–6 h) the amount of CO groups formed is negligible in comparison with the formation of polyene structures. The kinetics of carbonyl group formation can be measured by i.r. spectroscopy (*Figures 9* and *10*) when the samples are irradiated for longer times (50–200 h). Polyenes[45–48] and carbonyl groups[49] do at least seem to be concentrated at sample surfaces under the same conditions. HCl has been found to accelerate carbonyl group formation during the photo-oxidation of PVC[38]. These results have been attributed to an HCl-catalysed conversion of *sec*-peroxy radicals (>CHOO·) into hydroxyl radicals (·OH) and carbonyl groups.

It has also been reported that the non-oxidative thermal dehydrochlorination of PVC is facilitated by preliminary photodegradation of the polymer[45,50]. The thermal degradation increases with decreasing wavelength of irradiation and is a result of the photolytic formation of thermally labile defect sites.

The rather low stability of PVC for thermal decomposition requires stabilization of the polymer during thermal processing. One of the commercially used thermostabilizers are metal stearates. These stabilizers have two functions[11–20,51]:

(i) Binding (neutralizing) of HCl and thus excluding its autocatalytic effect:

$$(C_{17}H_{35}COO)_2Me + 2HCl \rightarrow 2C_{17}H_{35}COOH + MeCl_2 \qquad (4)$$

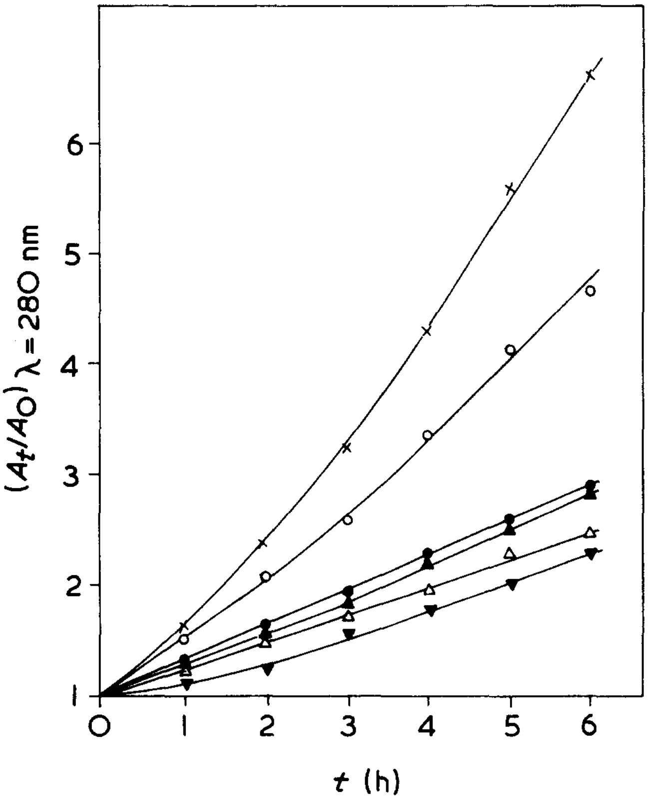
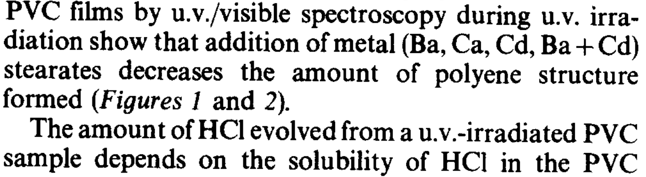


Figure 2 Kinetic curves for formation of polyene structures (n =3–4) in PVC containing 2.5×10^{-3} M metal stearates or stearic acid per 100 g of PVC during u.v. irradiation in air: ●, Ca stearate; ▲, Cd stearate; △, Ba stearate; ▼, Ba+Cd stearates; ○, stearic acid; compared with X, pure PVC

It was also realized[51,52] that the metal chlorides may accelerate the dehydrochlorination of PVC. $ZnCl_2$ is the most active metal halide in that connection followed by $CdCl_2$, whereas $BaCl_2$ and $CaCl_2$ are not active[51].

(ii) Exchanging labile chlorine atoms (allylic chlorines) and thus eliminating initiation sites:



$$-CH_2-CH=CH-\underset{\displaystyle Cl}{\underset{|}{C}H}-CH_2- + (C_{17}H_{35}COO)_2Me \rightarrow$$
$$-CH_2-CH=CH-\underset{\displaystyle OCOC_{17}H_{35}}{\underset{|}{C}H}-CH_2- + MeCl_2 \qquad (5)$$

It is important to examine the role of metal stearates in the photo-oxidative degradation of PVC in the solid state. Measurements of the formation of polyene structures in PVC films by u.v./visible spectroscopy during u.v. irradiation show that addition of metal (Ba, Ca, Cd, Ba + Cd) stearates decreases the amount of polyene structure formed (*Figures 1* and *2*).

The amount of HCl evolved from a u.v.-irradiated PVC sample depends on the solubility of HCl in the PVC matrix. The solubility of the HCl evolved in PVC causes an 'induction period' (*Figures 3* and *4*) depending on film thickness and experimental conditions. The amount of HCl which is formed in the polymer matrix can be measured by conductimetric methods only after migration through to upper layers of the u.v.-irradiated film.

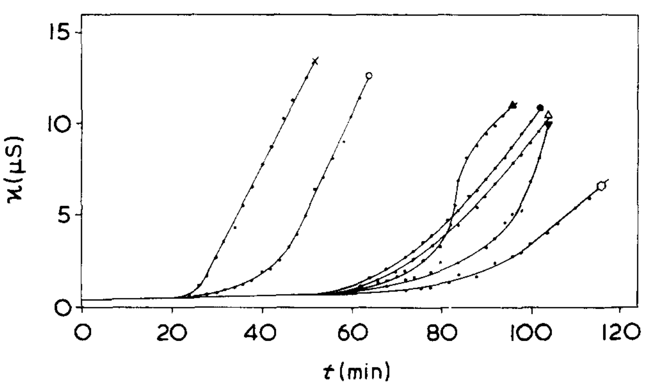


Figure 3 Kinetics of the formation of HCl expressed as conductivity units (μS) during u.v. irradiation of PVC films (0.5 g) in air: X, pure PVC; and PVC with 2.5x10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▲, Cd stearate; ●, Ca stearate; △, Ba stearate; ▼, Ba+Cd stearates; ⬡, Pb stearate; ○, stearic acid

These effects are comparable only with very thin films (~50 μm) of the same known thickness. Addition of metal (Ba, Ca, Cd, Pb, Ba + Cd) stearates gives an increase in the observed 'induction period'.

The results show the role of metal (Ba, Ca, Cd, Pb, Ba + Cd) stearates on the formation of polyene structures (*Figures 1* and *2*) and the evolution of HCl (*Figures 3* and *4*) during u.v. irradiation of PVC samples. It has also been found that pure stearic acid has a similar effect but much less than its metal salts (*Figures 1–4*).

On the other hand, metal (Ba, Ca, Cd) stearates accelerate the photo-oxidation of PVC (*Figure 5*). The oxygen uptake increases in the presence of added stearates. A straight line is produced when the logarithm of oxygen uptake rate is plotted against the reciprocal of the absolute temperature (*Figure 6*). From these measurements the energy of activation of photo-oxidation of PVC in the presence of added metal stearates was calculated: Ba + Cd 36.2×10^3 J, Cd 31.1×10^3 J, Ba 29.6×10^3 J, Ca 28.0×10^3 J; in comparison to pure PVC 38.5×10^3 J and in the presence of stearic acid 40.4×10^3 J. These results show that metal stearates decrease the energy of activation of photo-oxidation of PVC whereas stearic acid increases it. Diffusion of oxygen into a PVC matrix is also a temperature-dependent rate phenomenon, but it does not affect the calculated energy of activation in the measured temperature interval (20°–50°C).

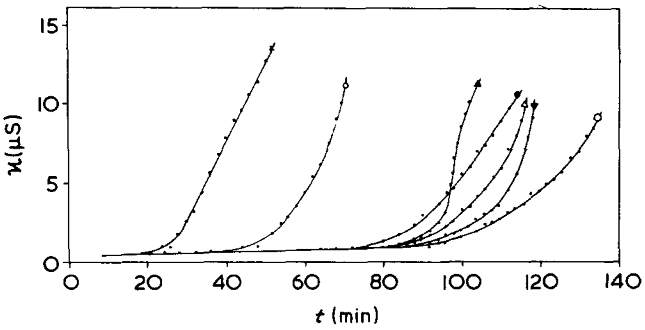


Figure 4 Kinetics of the formation of HCl expressed as conductivity units (μS) during u.v. irradiation of PVC films (0.5 g) in air; X, pure PVC; and PVC with 5x10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▲, Cd stearate; ●, Ca stearate; △, Ba stearate; ▼, Ba+Cd stearates; ⬡, Pb stearate; ○, stearic acid

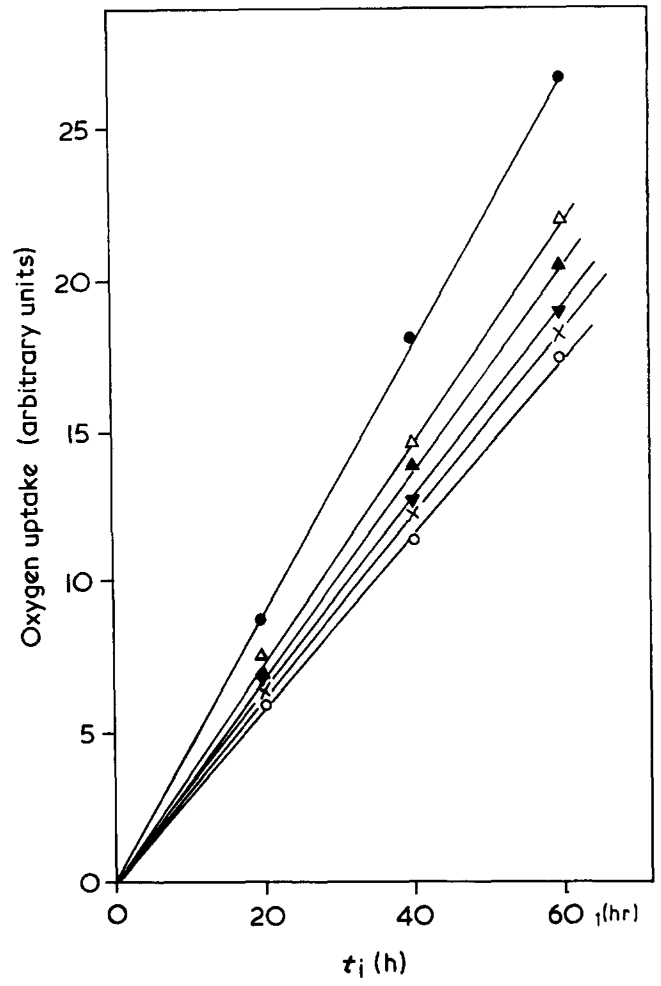
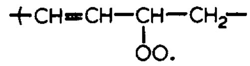


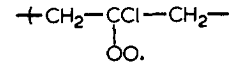
Figure 5 Oxygen uptake during u.v. irradiation of pure PVC (X) and PVC with 2.5x10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▼, Ba+Cd stearates; ▲, Cd stearate; △, Ba stearate; ●, Ca stearate; ○, stearic acid

The formation of hydroperoxy (OOH) (*Figures 7* and *8*) and carbonyl (CO) (*Figures 9* and *10*) groups increases rapidly with increasing concentration of added metal stearates.

The major oxidation processes involve primarily allylperoxy radicals


$$-\!\!\!\!+CH{=}CH-\underset{\displaystyle OO\cdot}{\underset{|}{CH}}-CH_2-CHCl+\!\!\!\!-$$

and α-chloroperoxy radicals


$$-\!\!\!\!+CH_2-\underset{\displaystyle OO\cdot}{\underset{|}{CCl}}-CH_2-CHCl+\!\!\!\!-$$

formed by the abstraction of tertiary hydrogens by peroxide radicals[23]. The peroxy radicals are formed from initial PVC radicals produced in the primary reactions in which metal stearates play an evident role. Because of the complete insolubility of metal stearates in common spectroscopic solvents, it is difficult to study their

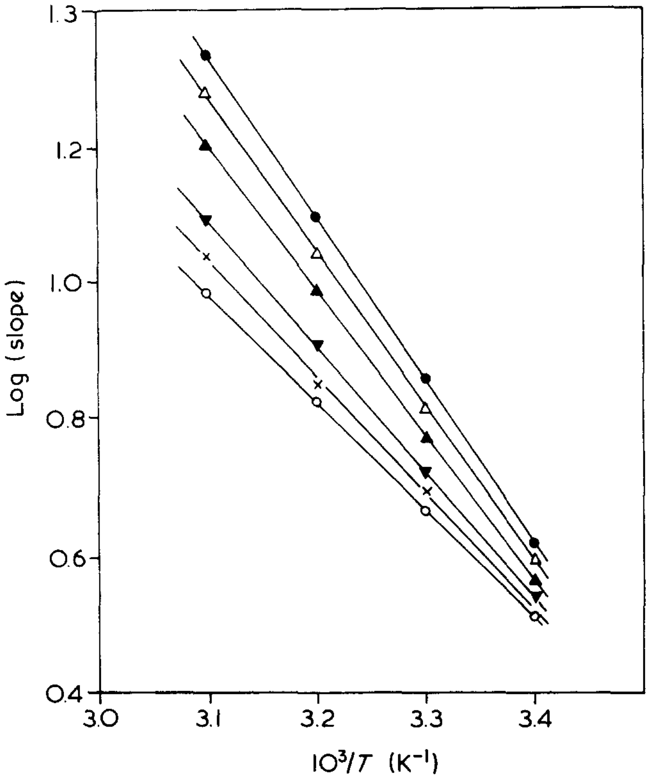


Figure 6 Activation energy of photo-oxidation of pure PVC (X) and PVC with 2.5x10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▼, Ba+Cd stearates; ▲, Cd stearate; △, Ba stearate; ●, Ca stearate; ○, stearic acid

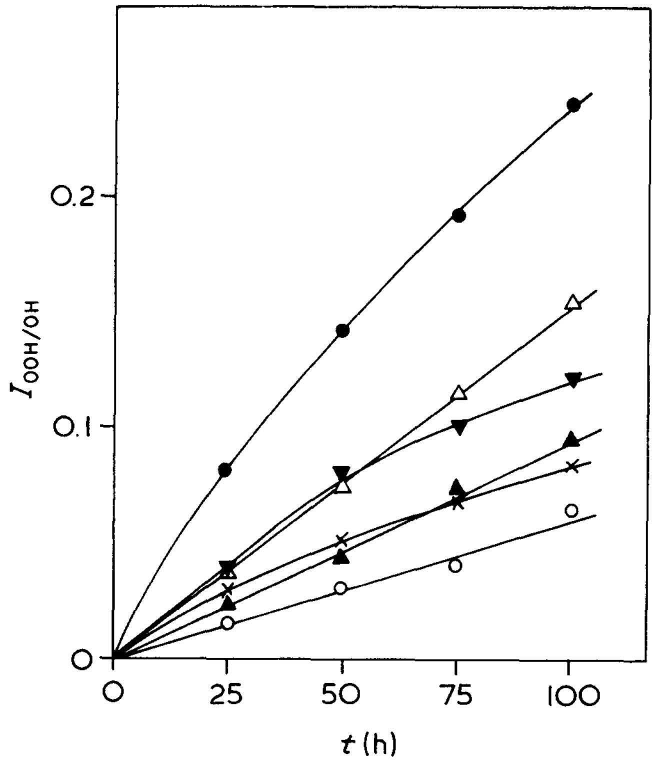


Figure 7 Kinetics of formation of hydroperoxy/hydroxyl (OOH/OH) groups in PVC during u.v. irradiation in air: X, pure PVC; and PVC with 2.5x10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▲, Cd stearate; ▼, Ba+Cd stearates; △, Ba stearate; ●, Ca stearate; ○, stearic acid

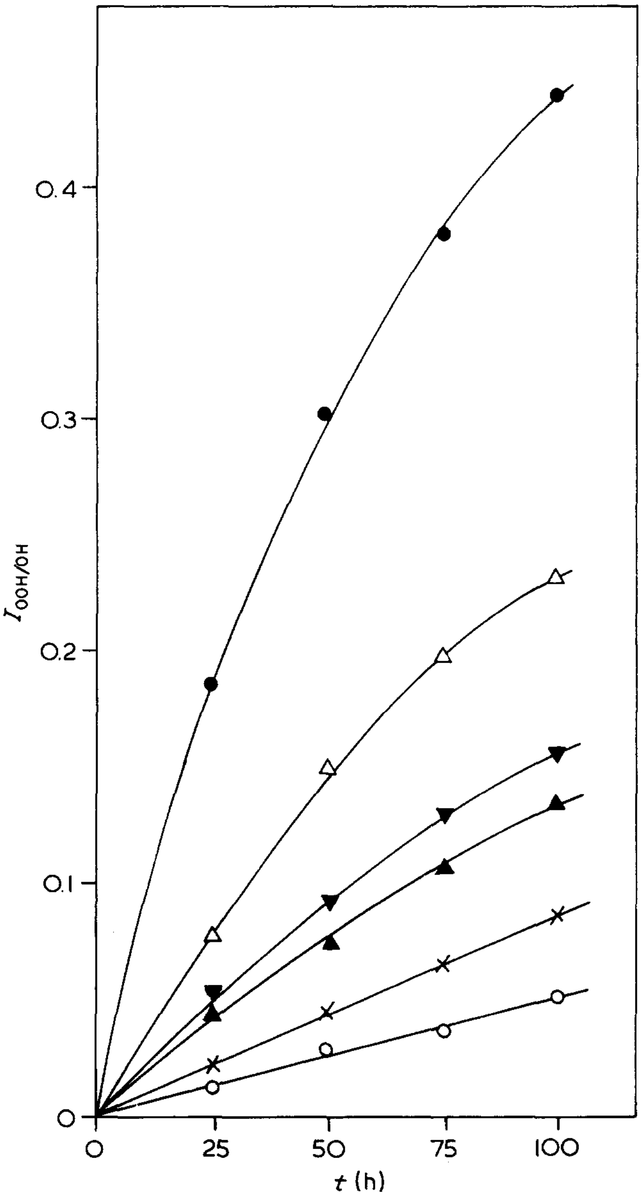


Figure 8 Kinetics of formation of hydroperoxy/hydroxyl (OOH/OH) groups during u.v. irradiation in air: X, pure PVC; and PVC with 5.0x10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▲, Cd stearate; ▼, Ba+Cd stearates; △, Ba stearate; ●, Ca stearate; ○, stearic acid

photoreactions. During u.v. irradiation of metal stearates in an e.s.r. cavity, we did not observe any measurable signal from free radicals formed. At present it is rather difficult to suggest a reasonable mechanism that would explain the accelerating effect of metal stearates on the photo-oxidation of PVC. Pure stearic acid has the opposite effect and decreases the amount of hydroperoxy (OOH) (*Figures 7* and *8*) and carbonyl groups (*Figures 9* and *10*) formed. It also increases the energy of activation of photo-oxidation of PVC from 38.5×10^3 J (for pure PVC) to 40.4×10^3 J. Stearic acid is almost completely photolysed by u.v. irradiation (*Figure 11*). At the wavelength 250–400 nm the energy absorbed by the acid is more than enough to rupture any of the bonds, R–COOH, RCOO–H or RCO–OH[53]. The radicals ·COOH and RCOO· are very unstable towards decomposition, whereas the radicals RCO· and ·OH are very reactive in

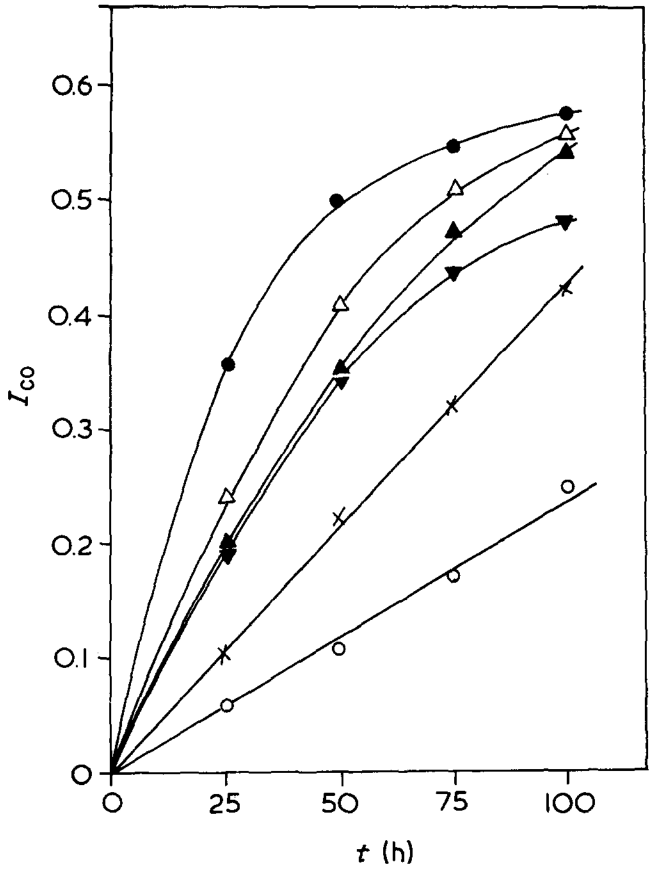


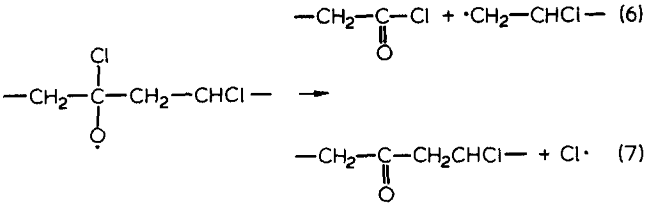
Figure 9 Kinetics of formation of carbonyl (CO) groups during u.v. irradiation in air: X, pure PVC; and PVC with 2.5x10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▼, Ba + Cd stearates; ▲, Cd stearate; △, Ba stearate; ●, Ca stearate; ○, stearic acid

addition to polymer alkyl and polymer allyl radicals and compete in this way with molecular oxygen.

In the case of Pb stearate added to PVC it was not possible even to measure u.v. and i.r. absorption spectra because of precipitation of $PbCl_2$ which made the u.v. irradiated PVC film milky and non-transparent to any kind of irradiation.

These results show the complex role of this type of additive in the photodegradation and photostabilization of PVC. Metal stearates decrease the HCl elimination but accelerate the photo-oxidation processes, and it is important to consider the contribution of both reactions on chain scission and crosslinking.

It is generally accepted that chain scission occurs by formation of hydroperoxides which yield α-chloroalkyl radicals, decomposed by a β-scission process (reaction (6)), either by cleavage of C–C bonds or by chlorine atom abstraction (reaction (7))[54]:



$$-CH_2-\underset{\underset{O^{\bullet}}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-CHCl- \rightarrow \begin{array}{ll} -CH_2-\underset{\underset{O}{\|}}{C}-Cl + {}^{\bullet}CH_2-CHCl- & (6) \\ -CH_2-\underset{\underset{O}{\|}}{C}-CH_2CHCl- + Cl^{\bullet} & (7) \end{array}$$

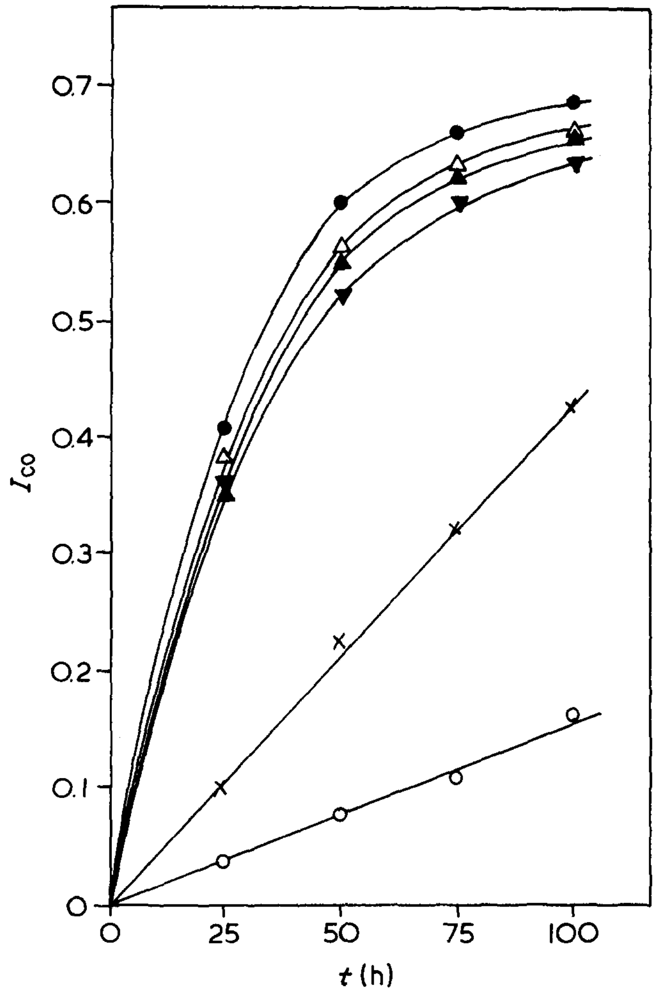


Figure 10 Kinetics of formation of carbonyl (CO) groups during u.v. uiradiation in air: X, pure PVC; and PVC with 5.0x10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▼, Ba + Cd stearates; ▲, Cd stearate; △, Ba stearate; ●, Ca stearate; ○, stearic acid

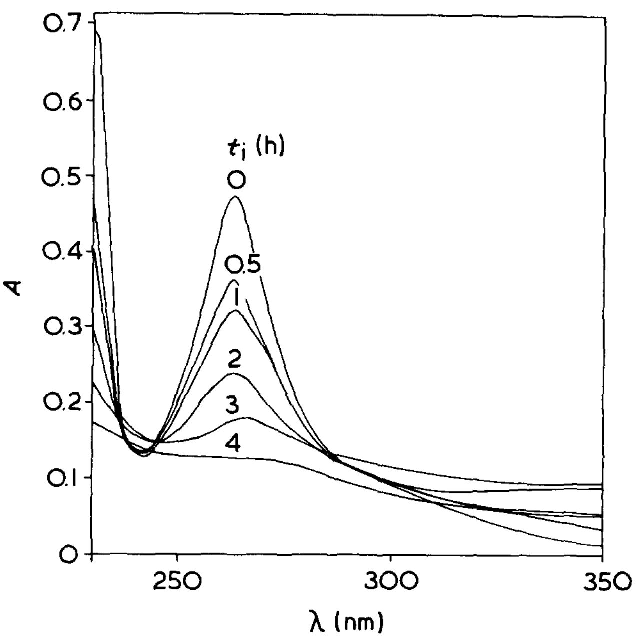


Figure 11 Change of u.v. absorption spectra of stearic acid in methanol (1.0x10^{-5} M) in air during u.v. irradiation at 254 nm

The additional production of propagating chlorine radicals accounts for the enhanced degradation in the presence of oxygen. It seems that metal stearates are responsible in some way for the additional production of propagating chlorine radicals during u.v. irradiation of PVC samples.

Chain scission and crosslinking occur simultaneously in the same u.v.-irradiated samples[54]. The gel content decreases in the presence of added metal stearates (*Figure 12*). Crosslinking may occur by the termination of different types of polymer alkyl, allyl, oxy and peroxy radicals and by addition of some radicals to the double bonds[55-57]. The role of metal stearates in decreasing crosslinking reactions is not well understood.

In conclusion, metal stearates have a stabilizing effect on photodehydrochlorination of PVC but at the same time they have an accelerating effect on the photo-oxidation of PVC. The observed accelerating effect is the result of decreasing the energy of activation of photo-oxidation caused by added metal stearates. From the experimental data, the following order of metal stearate activity can be proposed:

(1) Stabilization of photodehydrochlorination: stearic acid < Cd stearate < Ca stearate < Ba stearate < (Ba + Cd) stearates (synergistic effect) < Pb stearate.

(2) Acceleration of photo-oxidation: Ca stearate > Ba stearate > Cd stearate > (Ba + Cd) stearates > stearic acid.

The synergistic effect of (Cd + Ba) stearates can be caused by an exchange reaction between metal chlorides and metal carboxylates, but the mechanism is not well understood[1,51,52]. It has been suggested that the Cd stearate reacts first with PVC and that the metal chloride formed then reacts with the Ba stearate regenerating the Cd stearate[13].

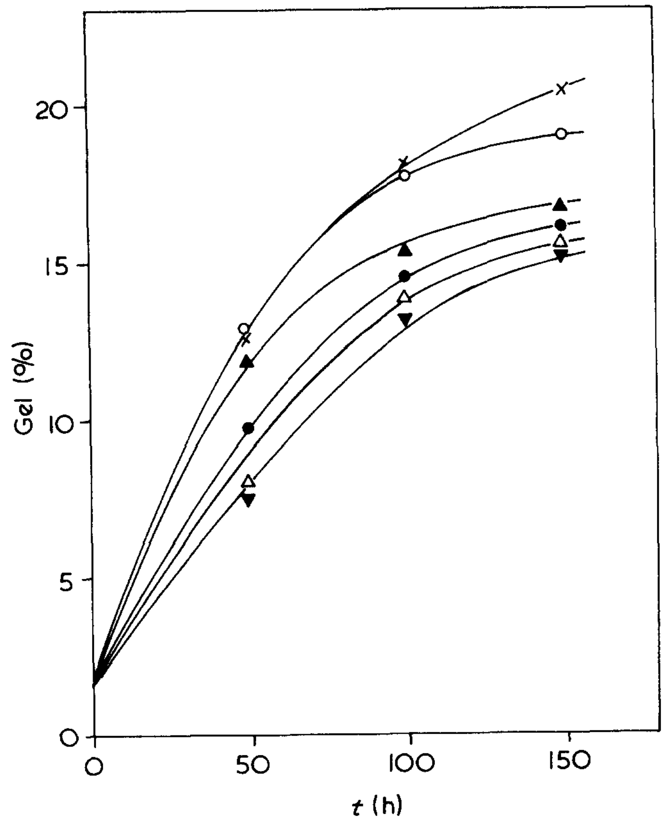


Figure 12 Kinetics of gel formation during u.v. irradiation in air: X, pure PVC; and PVC with 2.5×10^{-3} M metal stearates or stearic acid added per 100 g of PVC: ▼, Ba+Cd stearates; △, Ba stearate; ●, Ca stearate; ▲, Cd stearate; ○, stearic acid

From a photochemical point of view, an optimum concentration is expected to be required for the thermal stabilization by metal stearates and any excess concentration should be avoided. Formation of polyene structures acts as a protective filter[45-48,58-62] and may in addition retard the rate of photo-oxidation by inhibiting the diffusion of molecular oxygen[63]. In some situations, polyene formation is a more acceptable process than photo-oxidation of PVC which gives formation of hydroperoxy (OOH) and carbonyl (CO) groups. The photo-oxidation of PVC frequently leads to a reduction in the formation of conjugated double bonds due to oxidation[64].

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