

Studies on the Photo-oxidation Mechanism of Polymers. VI. The Role of Commercial Thermostabilizers in the Photostability of Poly(vinyl Chloride)*

J. F. RABEK,[†] G. CANBÄCK, and B. RÅNBY, *Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden*

Synopsis

This paper presents a study on the photolysis of PVC in the presence of different types of tin stabilizers. Using physicochemical methods such as ESR spectroscopy, conductivity titration, gel permeation chromatography, and absorption spectroscopy, the mechanism of PVC photolysis has been investigated. ESR spectroscopy shows that during UV irradiation of tin stabilizers, different types of free radicals depending on the chemical structure of the examined compounds are formed. It has been found that the presence of tin stabilizers does not significantly influence the photo-oxidation and degradation of PVC but influences the crosslinking processes. The authors propose an interpretation of the free-radical formation during UV photolysis of tin stabilizers and of the crosslinking acceleration mechanism.

INTRODUCTION

Poly(vinyl chloride) (PVC) tends to decompose thermally at common molding temperatures (175–200°C). To be used in finished articles, PVC needs stabilization against thermal degradation. Organotin compounds have a wide application as thermal stabilizers for PVC because they stabilize for long periods of time at high temperatures. They are compatible with the polymer, giving clear and rigid products. There are different theories for the mechanism of thermal stabilization,¹⁻⁶ and the problems are not yet solved.

The wide application of PVC as a construction material in the building and machine industries requires photostability outdoors for several years. Effects of additives like thermal stabilizers on the natural and photo-induced aging of PVC have not been widely investigated.⁷ In order to improve the photostability of commercial products made from PVC, it is necessary to study systematically the influence of different additives on the photo-oxidation of PVC. It is necessary to observe that the incorporation of any functional compound into PVC for a certain purpose may have additional effects on the photolysis and other

* Presented at IUPAC Symposium on Photochemical Processes in Polymer Chemistry, Leuven, Belgium, June 2-4, 1976.

[†] Previous address: Instytut Technologii Organicznej i Tworzyw Sztucznych, Politechniki Wrocławskiej, Wrocław, Poland.

photo-oxidation processes. When a compound is added to PVC, its stability can be influenced in two directions. The additives, or products of their photolysis, may accelerate the photoreactions of PVC. The additives may also retard photolysis by radical scavenging and deactivation of excited groups in the polymer or its impurities.

Studies of these processes should make it possible to select various additives also from a photochemical point of view and to choose those of low sensitivity to UV light. This is important in the efforts to obtain a general improvement of the light stability in commercial PVC products. Concerning photolysis and photo-oxidation of PVC, there is a tendency to use stabilizers which have anti-oxidant properties and which are able to terminate the radical chain processes which may occur during photodegradation. We have started this research with a study of tin stabilizers of the general structure R_2SnY_2 , where R usually is an alkyl group and Y a mercapto or ester group or some modification thereof.

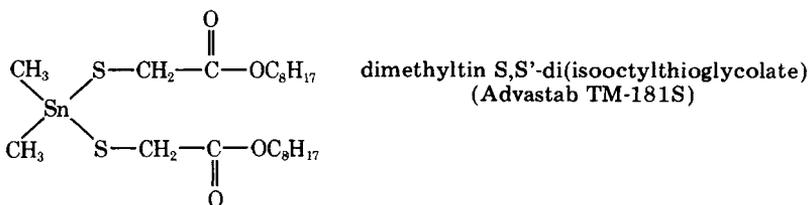
EXPERIMENTAL

Suspension-polymerized PVC (Pevikon S-602) was obtained from KemaNord AB (Sweden) in the form of a white powder. The following specifications were given by the manufacturer: Fikentscher *K* value 60, $\overline{M}_n = 46\,000$, and $\overline{M}_w = 103,000$, i.e., polydispersity factor 2.2.

The polymer was purified by extensive extraction of the PVC powder in ethanol (99.9%) for about one week, applying vigorous stirring, followed by filtration and drying under vacuum at room temperature. Our previous studies⁸ have shown that residues of tetrahydrofuran (THF used as solvent) are very difficult to remove. Traces of THF were found to accelerate the photo-oxidative degradation of the polymer.⁸

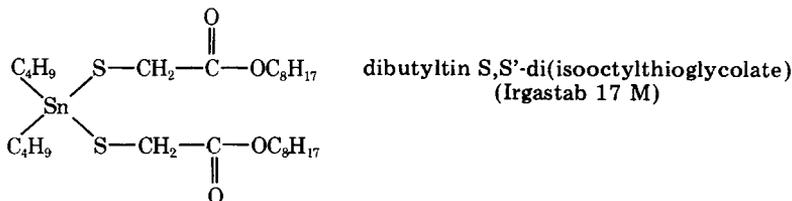
Our choice of the organotin stabilizers to be used was based upon the following considerations: (i) the stabilizers should be representative of the various important types used industrially; (ii) their molecular structure should be known and well established and give photostability for comparison of the results in the groups examined. The following tin stabilizers of the type R_2SnY_2 have been chosen:

Group A:



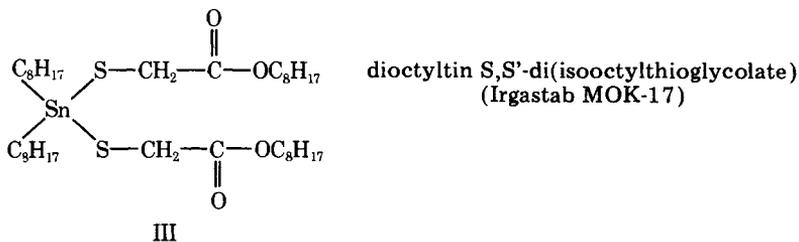
dimethyltin S,S'-di(isooctylthioglycolate)
(Advastab TM-181S)

I

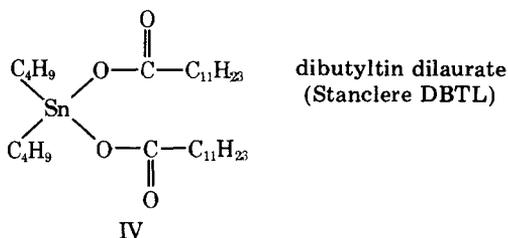


dibutyltin S,S'-di(isooctylthioglycolate)
(Irgastab 17 M)

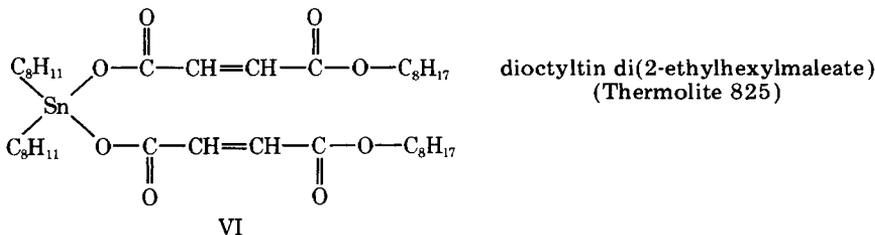
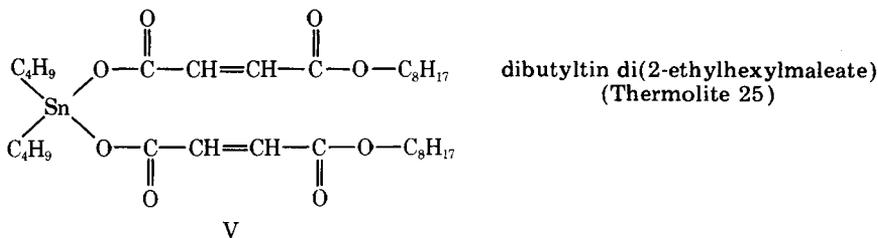
II



Group B:



Group C:



The tin stabilizers were used as delivered from the producers without any further purification. They are added and mixed with the PVC powder (1:100), the mixture was dissolved in CH_2Cl_2 , and films of 50–70 μm thickness were then cast by solvent evaporation.

A mercury lamp, Type HPK 125 W, from Philips (The Netherlands), giving mainly 2537 Å radiation, was used for short (1–6 hr) UV exposures. For long UV exposures (100 hr), a photoreactor, Type RPR-208 Rayonet with eight lamps of 125 W Type RUL, 2537 Å, was used. All irradiations were carried out at room temperature.

Samples for ESR measurement were irradiated under vacuum at -196°C in rotating, sealed quartz tubes of 4 mm diameter placed in a Dewar with quartz finger. To remove air from the samples, a vacuum line (10^{-5} mm Hg) was used for repeated evacuations. ESR spectra were recorded with an X-band spectrometer (Model JES-ME-1X from the Japan Electron Optics Laboratory Co. Ltd) operated with 100-kHz field modulation. A cylindrical TE_{011} cavity was used. The majority of the ESR spectra were recorded with variable-temperature accessories attached to the spectrometer.

UV absorption spectra of thin PVC films and solutions of tin stabilizers in methanol (spectrally pure) were obtained with a Beckman DK-2A spectrometer, and IR-absorption spectra of PVC films were obtained in a Perkin-Elmer 257 spectrometer.

The gel content of the PVC was measured by extracting 0.2 g (W_1) with THF for 24 hr in a Soxhlet apparatus equipped with coarse Alundum thimbles (RA98) 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 $100 (W_2/W_1)$.

Determination of the molecular weight distribution of the PVC samples was made by gel permeation chromatography (GPC) using a Waters Associates Instrument Model 200 as described earlier,⁸ with purified THF as solvent.

Measurements of HCl formed in the liquids during the photolysis of PVC were made by conductivity titration with 0.01 N NaOH.

RESULTS

By applying the three main variations of structure (groups A, B, and C) in the tin stabilizers used for this work, we obtained large amounts of experimental data. The presentation required selection, and we only present some of the typical results in this paper.

UV absorption spectra of the tin stabilizers used are given in Figure 1. The spectra do not show absorption peaks characteristic of carbonyl groups. Solutions containing 1 wt-% (this is the minimum concentration of thermostabilizers in commercial products of PVC) completely absorb light below 300 nm, and the absorption also extends into the visible region (Fig. 1). During UV irradiation of tin stabilizer solutions in methanol with light of 2537 Å, photolytic reactions occur. In the case of tin stabilizers of group A (I–III) (Fig. 2) and group C (V and VI) (Fig. 3), first a decrease and then an increase of absorption is observed. For the stabilizer of group B (IV) (Fig. 4), the increase in absorption occurs from the start of UV irradiation.

ESR spectra of free radicals formed during UV irradiation of some of the examined tin stabilizers are shown in Figures 5, 6, and 7. Addition of tin stabilizers (I–VI) to PVC (1 wt-%) causes a decrease in the rate of dehydrochlorination (Fig. 8) and in the rate of formation of polyene structures (Fig. 9) during UV irradiation.

Addition of tin stabilizers to PVC (1 wt-%) does, however, increase the rate of formation of a broad peak at $3600\text{--}2500\text{ cm}^{-1}$ (attributed to peroxy and hydroxyl groups) and a peak at $1800\text{--}1700\text{ cm}^{-1}$ (attributed to carbonyl and carboxyl groups) (Fig. 10). The hydroxyl and carbonyl bands increase at a constant rate for all tin stabilizers (I–VI) examined.

Gel permeation chromatography (GPC) indicates a decrease of molecular weight with increasing times of UV irradiation, presumably as a result of carbonyl group formation and subsequent chain scission. PVC samples containing tin stabilizers (1 wt-%) of compounds I–VI after UV irradiation and after separation of the crosslinked part as gel have no visible change in shape and position of the molecular weight distribution curve, compared with irradiated PVC samples free from thermal stabilizers.

The gel content (in wt-%) increases to different degrees depending on which

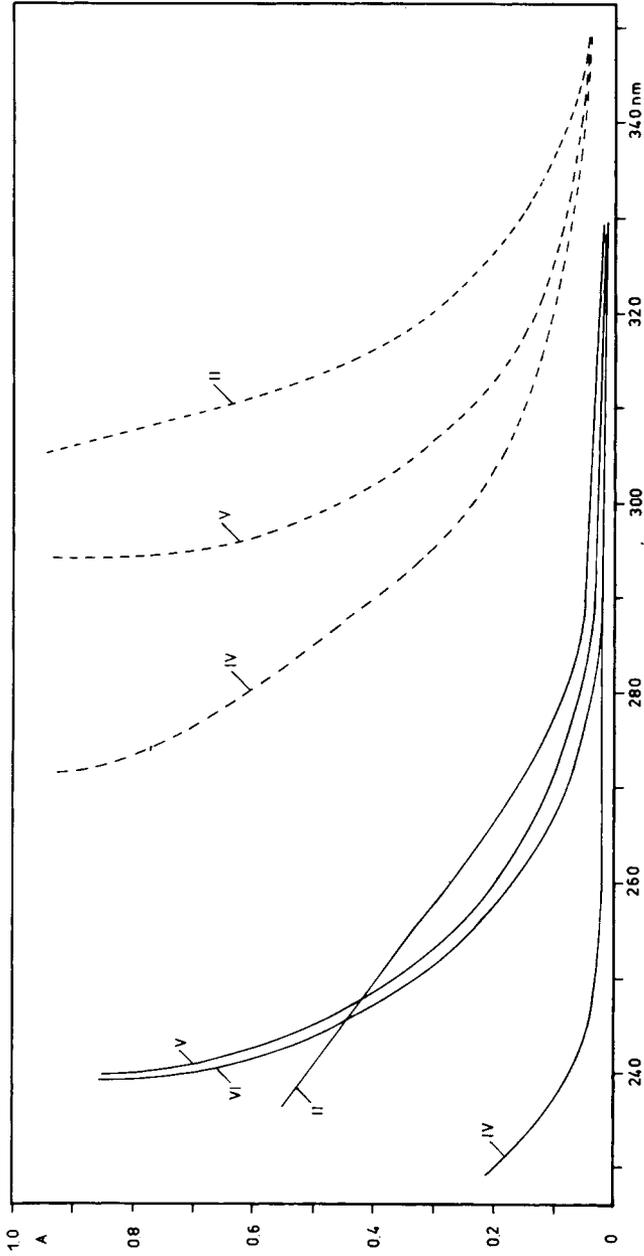


Fig. 1. UV absorption spectra of some tin stabilizers in methanol at the following concentrations: solid lines, 0.01 wt-% (7.915×10^{-2} g/l); dotted line, 1.0 wt-% (7.915 g/l).

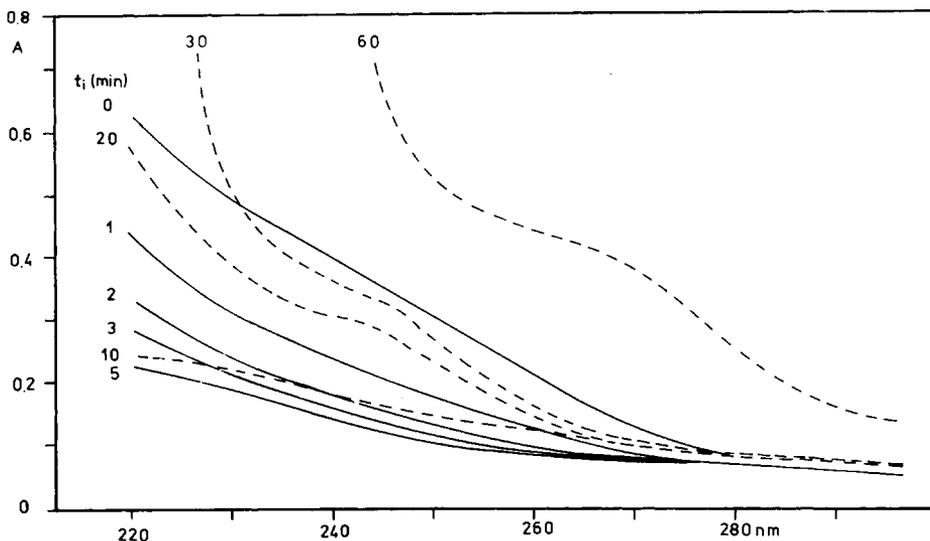
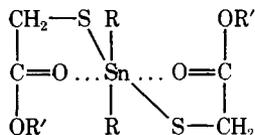


Fig. 2. Kinetics of changes in UV absorption spectra of tin stabilizer III in methanol (7.155×10^{-2} g/l.) during UV irradiation (min).

group of tin stabilizers is added, e.g., group A and C (60–80 wt-%) group B (50 wt-%), in comparison with pure PVC (20–30 wt-%) after 6 hr of UV irradiation.

DISCUSSION OF RESULTS

Tin stabilizers of the type R_2SnY_2 studied here show internal coordination of carbonyl groups with the tin atom as shown for dialkyltin *S,S'*-di(isooctylthioglycolate):



The coordination of carbonyl groups influences the light absorption of tin stabilizers in such a way that they do not show the characteristic absorption peak at about 280 nm for this group (Fig. 1).

When the tin stabilizers are UV irradiated, excitation of carbonyl groups to triplet states may occur. An electronically excited molecule may undergo more than one primary photochemical reaction. The most probable reaction is dissociation into free radicals, which is supported by the results from ESR measurements.

ESR studies of the radicals formed during UV irradiation of the tin stabilizers I–VI and the decay of these radicals when the samples are warmed show the presence of different types of radicals. Stabilizers of group A (I–III) containing the same central group at the Sn atom, but with alkyl groups of different lengths, all show the same ESR spectra after 20 min of UV irradiation and the same behavior on thermal treatment (Fig. 5). From the decay behavior, it is clear that at least two types of radicals are present. The fact that stabilizers I–III give

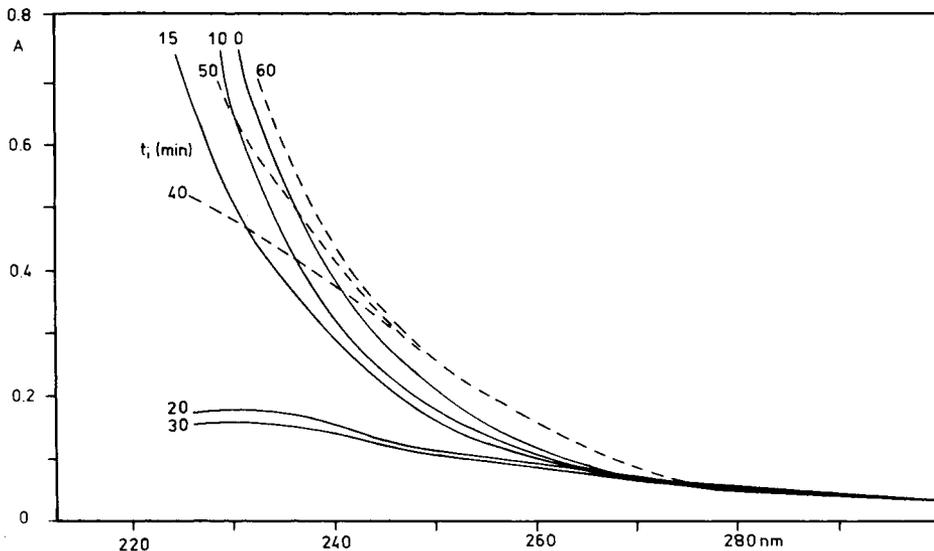


Fig. 3. Kinetics of changes in UV absorption spectra of tin-stabilizer VI in methanol (7.13×10^{-2} g/l.) during UV irradiation (min).

identical ESR spectra makes it probable that the radicals are formed by cleavage within the Y group (S—CH₂—CO—O—C₈H₁₇). In the ESR spectra, no signals typical for R—S· radical can be observed.

We tentatively propose a reaction mechanism for UV photolysis of tin stabilizers which involves formation of acyl radicals (1) and oxy radicals (2)

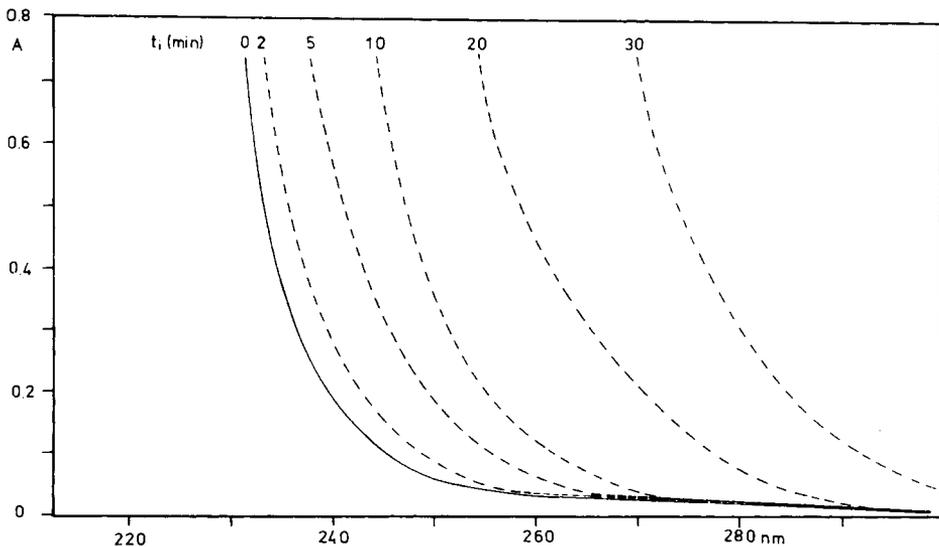
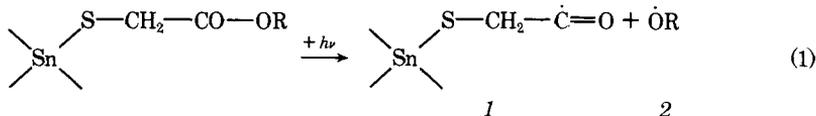


Fig. 4. Kinetics of changes in UV absorption spectra of tin stabilizer IV in methanol (7.91×10^{-1} g/l.) during UV irradiation (min).

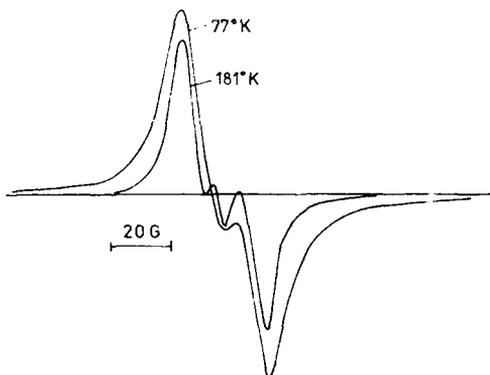
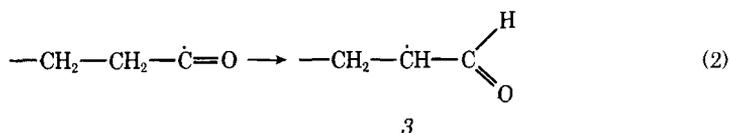


Fig. 5. ESR spectrum from UV-irradiated (20 min) tin stabilizer II at 77°K and after warming to 181°K for 5 min.

It has been shown by Tsuji⁹ that acyl radicals of type 1 can be converted to radical of type 3:



Attempts to detect carbon monoxide by gas chromatography after photolysis of thermostabilizers were unsuccessful.

If the photolysis of a tin stabilizer of group B (IV) occurs by a similar mechanism as that of group A, we can expect the following free radicals:

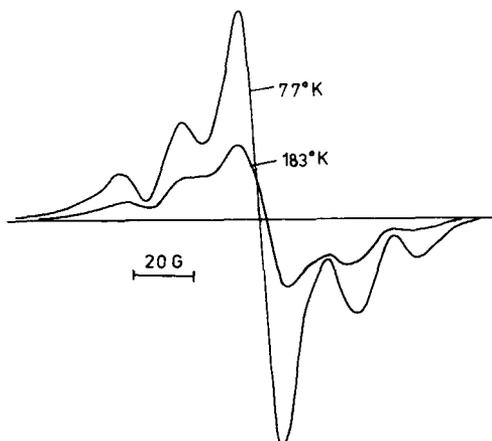
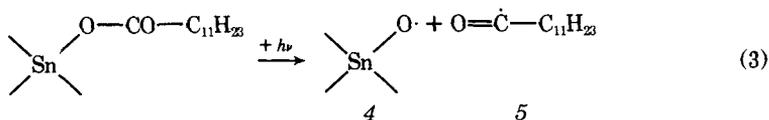


Fig. 6. ESR spectrum from UV-irradiated (120 min) tin stabilizer IV at 77°K and after warming to 183°K for 5 min.

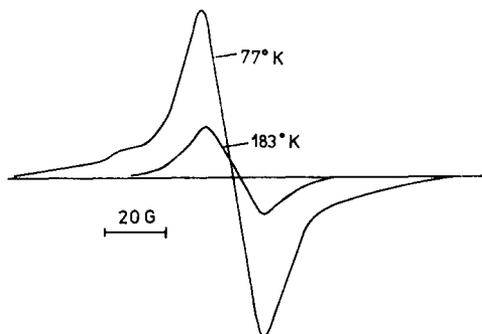


Fig. 7. ESR spectrum from UV-irradiated (120 min) tin stabilizer VI at 77°K and after warming to 183°K for 5 min.

Tin-oxo radical (4) may cause the main part of the central peak in Figure 6 (with $\Delta H_{msl} \approx 19$ G), and radicals 5 and 3 form the remaining part of the spectrum.

Tin stabilizers of group C (V–VI) give similar ESR spectra of different intensities. The ESR signal from stabilizer VI has a larger number of spins than that of V. Assuming the previously proposed mechanism for photolysis of tin stabilizers of group A and group B, we can expect the following radicals, depending on which carbonyl group is excited:

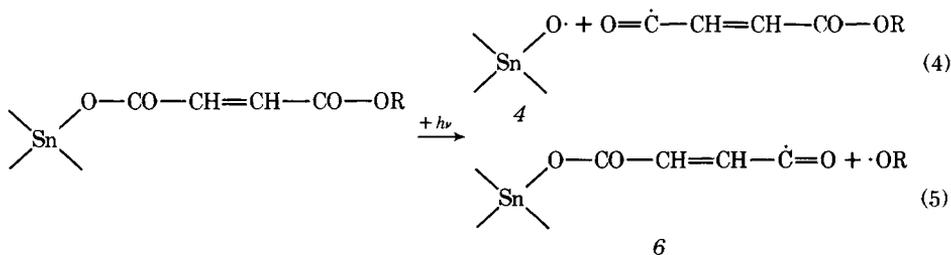


Figure 7 supports the assumption that the broad single-line spectrum may be attributed to the tin oxy radicals 4 rather than to radicals 6.

Study of the kinetics of the photolysis of different tin stabilizers in methanol solutions shows that the decomposition rate of these compounds depends on their molecular structure (Figs. 2–4). At the beginning of the UV irradiation of tin stabilizers of groups A and C, we observed a decrease in the UV absorption; but after prolonged UV irradiation, the absorption increased. For tin stabilizer VI from group C, we observed a rapid change in absorption after 15 min of UV irradiation (Fig. 3) which can be caused by an autocatalytic reaction. During UV irradiation of tin stabilizer IV (group B), we only observed an increase in UV absorption during photolysis (Fig. 4). These results show that the mechanism of photolysis depends on the stabilizer structure and is rather complicated. From experiments, it was evaluated that the light stability of the examined tin stabilizers can be written in the following order: group B (IV) > group C (V, VI) > group A (I, II, III).

During long-time (100 hr) UV photolysis of tin stabilizers from group A, we observed precipitation of stannous sulfide (SnS); but in the presence of HCl, stannic chloride (SnCl₄) is formed. The mechanism of photolysis of tin stabilizers is complex and can not yet be presented here in detail.

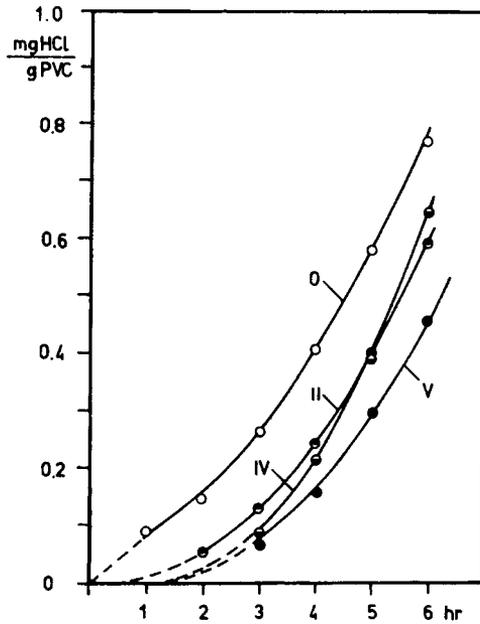


Fig. 8. Kinetics of dehydrochlorination of PVC (0 = pure) and in the presence of different tin stabilizers: II, IV, and V.

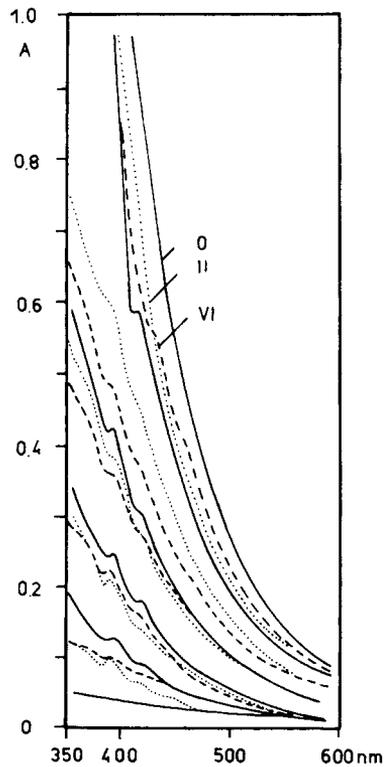


Fig. 9. Kinetics of changes in visible absorption spectra of PVC (0 = pure) and in the presence of tin stabilizers (1.0 wt-%).

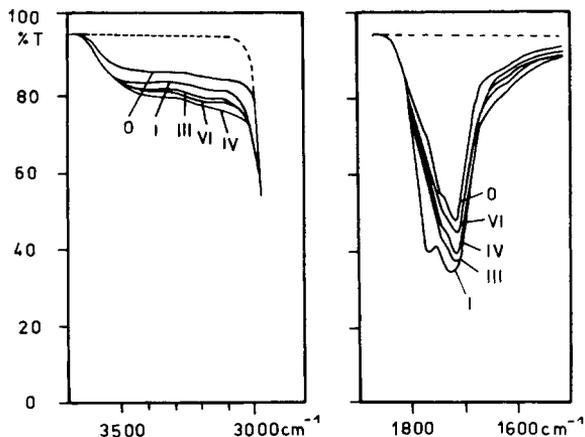
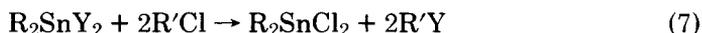
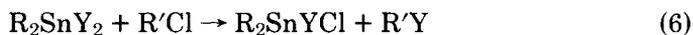


Fig. 10. IR-absorption spectra of PVC films (0 = pure) and in the presence of different tin-stabilizers (1.0 wt-%).

From the polymer stabilization point of view, it is important to determine the role of photolysis of thermostabilizers on the stability of PVC. It is well known that during UV irradiation of PVC, a dehydrochlorination process is observed.^{10,11} Simple HCl evolution rates give little information about the rates of initiation and termination of the degradation processes. The presence of tin stabilizers in PVC samples gives an induction period during which evolution of HCl during photolysis is decreased (Fig. 8). After this period, the rate of loss of HCl from the polymer is approximately the same as the rate of dehydrochlorination for the unstabilized polymer. Approximately four moles of HCl per one mole of tin stabilizer added was consumed.

Studies of thermal stabilization of PVC¹²⁻¹⁵ show that tin stabilizers provide maximum stabilization for PVC by eliminating labile sites that may initiate dehydrochlorination, by acting as HCl scavenger, by reacting with free radicals as they are formed, and by acting as antioxidants. Onozuka¹⁶ has confirmed that organotin stabilizers react with model compounds which represents the active chlorine atoms on allylic and tertiary sites in the polymer chain. Commercial PVC probably has both tertiary hydrogen and tertiary chlorine, but the relative amounts are difficult to determine. The mechanism for thermal stabilization proposes a replacement of labile chlorine atoms on the polymer chains by Y groups leading to a structure with enhanced thermal stability:



It has been shown that tin stabilizers of group A (I-III) react with hydrogen chloride liberated from PVC.^{13,17} The alkyl groups (R) of tin stabilizers also react with free radicals formed from PVC degradation. A tin stabilizer with one alkyl group left can further react with other radicals or double bonds in the polymer chain.

The presence of tin stabilizers retards the development of visible discoloration by decreasing the formation of polyene structure (Fig. 9), but apparently increase the crosslinking process. On the other hand, tin stabilizers do not significantly

ditives such as waxes, antioxidants, photostabilizers, pigments, etc., and what other effects they have on the light stability of PVC. This problem is very complex and requires further stepwise research.

These investigations are part of a research program on photo-oxidation and photostabilization of polymers supported by the Swedish Board for Technical Development (STU) and the Swedish Polymer Research Foundation (SSP). The authors thank Ing. E. Walldén for his unfailing efforts in carrying out the hundreds of experiments required and to Norsk Hydro A/S, Porsgrunn, Norway, KemaNord AB, Sundswall, Sweden, and M&T International NV, Vlissingen-Ooost, The Netherlands, for supplying the different kinds of tin stabilizers.

References

1. F. Chevassus and R. de Broutelles, Eds., *The Stabilization of Polyvinyl Chloride*, Arnold, London, 1963.
2. B. W. Rockett, M. Hadlington, and W. R. Poyner, *J. Appl. Polym. Sci.*, **17**, 3457 (1973).
3. A. H. Frye, R. W. Horst, and M. A. Paliobagis, *J. Polym. Sci. A2*, **2**, 1765, 1785, 1801 (1964).
4. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).
5. A. Ross, *Ann. New York Acad. Sci.*, **125**, 177 (1967).
6. G. Ayrey, R. C. Poller, and I. H. Siddiqui, *J. Polym. Sci. B*, **8**, 1 (1970).
7. G. Scott and M. Tahan, *Eur. Polym. J.*, **11**, 535 (1975).
8. J. F. Rabek, Y. J. Shur, and B. Rånby, *J. Polym. Sci.*, **A1**, 1285 (1975).
9. K. Tsuji and T. Seiki, *J. Polym. Sci. B*, **10**, 185 (1972).
10. B. Rånby and J. F. Rabek, *Photodegradation, Photo-oxidation, and Photostabilization of Polymers*, Wiley, London, 1975.
11. J. F. Rabek, G. Canbäck, J. Lucky, and B. Rånby, *J. Polym. Sci., Polym Chem. Ed.*, **14**, 1447 (1976).
12. A. S. Kenyon, *NBS Circ.* **525**, 81 (1963).
13. P. P. Klemchuk, *Advan. Chem. Ser.*, **No. 85**, 1 (1968).
14. T. Suzuki, I. Takakura, and M. Yoda, *Eur. Polym. J.*, **7**, 1105 (1971).
15. G. Ayrey, R. C. Poller, and I. H. Siddiqui, *J. Polym. Sci. A1*, **10**, 725 (1972).
16. M. Onozuka and M. Ashina, *J. Macromol. Sci.*, **C3**, 235 (1968).
17. G. C. Marks, J. L. Benton, and C. M. Thomas, *SCI Monograph*, **19**, 204 (1967).

Received March 30, 1976

Revised July 8, 1976