The Action of Tridecyl Phosphite in the Stabilization of Poly(vinyl chloride) with Metal Soaps
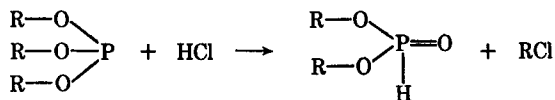
F. J. HYBART and G. N. ROWLEY,* *Chemistry Department,*
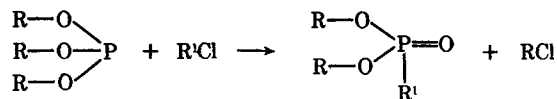*The University of Aston in Birmingham, Birmingham B4 7ET, England*

Synopsis

The effect of tridecyl phosphite on the stabilization of the thermal degradation of poly(vinyl chloride) under nitrogen by cadmium and zinc stearates has been studied. The rate of evolution of hydrochloric acid from solutions of the polymer with stabilizers in dioctyl phthalate at 190°C has been measured. Tridecyl phosphite absorbs HCl and is converted into the phosphonate which reduced the deleterious action of the cadmium and zinc chlorides formed from the stearates.

INTRODUCTION

The thermal degradation of poly(vinyl chloride) with the evolution of HCl by a zipper mechanism leads to the formation of a polyene structure.[1–4] This degradation is reduced by the addition of metal soaps. Since this reaction is catalyzed by the HCl evolved, one of the functions of the stabilizer is to absorb the HCl and reduce the autocatalytic reaction.[4] However, the metal chloride that is formed can accelerate the degradation reaction by a Friedel-Craft-type reaction so that cadmium stearate is more effective than zinc stearate. The metal stearate probably has some other function as well as that of removing HCl from the system. Esterification of the poly(vinyl chloride) at the polyene sequence has been suggested.[4] When organic phosphites are added to poly(vinyl chloride) without metal soap, they do not improve the stability when measured by the formation of color within the sample. However, they aid the stabilization by metal soaps and are thought to chelate with the metal chloride, reducing its deleterious effect.[6] Phosphites can also (1) react with hydrochloric acid,

$$
\begin{array}{c}
\text{R—O} \\
\text{R—O—P} \\
\text{R—O}
\end{array}
+ \text{HCl} \longrightarrow
\begin{array}{c}
\text{R—O} \\
\text{R—O—P=O} \\
\quad\quad\;\; | \\
\quad\quad\;\; \text{H}
\end{array}
+ \text{RCl}
$$

to form a phosphonate,[6] and (2) undergo the Michaelis-Arbusov rearrangement[7]:

$$
\begin{array}{c}
\text{R—O} \\
\text{R—O—P} \\
\text{R—O}
\end{array}
+ \text{R}^1\text{Cl} \longrightarrow
\begin{array}{c}
\text{R—O} \\
\text{R—O—P=O} \\
\quad\quad\;\; | \\
\quad\quad\;\; \text{R}^1
\end{array}
+ \text{RCl}
$$

* Present address: Chemistry Department, University of Lancaster, Lancaster, England.

This reaction could occur with poly(vinyl chloride) if R'Cl is a segment of the polymer chain.   Such a reaction may modify the formation of polyene sequences, particularly if the reaction is favored by the presence of a C=C double bond.

EXPERIMENTAL

Apparatus

The hydrogen chloride evolved during the thermal degradation of poly(vinyl chloride) was measured by a continuous acid base titration.[8]   Dry, oxygen-free nitrogen was passed through a solution of 0.2 g poly(vinyl chloride) in di-2-ethylhexyl phthalate (6 ml) at 190°C and with stabilizers added as required.   Any hydrogen chloride formed was swept out of the reaction cell by the nitrogen and was continuously titrated against standard sodium hydroxide solution.

Materials

Poly(vinyl chloride) was supplied by I.C.I. Ltd. (Plastics Division) and had been prepared by a suspension polymerization.   The average molecular weight determined by its solution viscosity in tetrahydrofuran was 51,000.

Di-2-ethylhexyl phthalate (DOP) was Hopkins and Williams Laboratory reagent and was used as supplied.

Zinc stearate, cadmium stearate, and triisodecyl phosphite were used as supplied by Victor Wolf Ltd., Manchester.   The purity of the triisodecyl phosphite was stated to be better than 95%, but no method for improving its purity could be developed.

Zinc and cadmium chloride were laboratory reagents (Hopkins & Williams) and were dried in an air oven and stored over concentrated sulfuric acid.

RESULTS

Experiments with Cadmium Salts

Many experiments were made with solutions of poly(vinyl chloride) at 190°C without stabilizers.   In each case, after a slow start, HCl was evolved at steady rates within 3% of a mean value of 3.0 μmoles g^{-1}min^{-1}. The evolution of HCl was then measured from poly(vinyl chloride) to which varying amounts of cadmium stearate had been added (Fig. 1).   The curvature at the bottom varies because all of the HCl is not absorbed immediately by the cadmium stearate.   After this initial period, the rates of evolution become steady at a lower level than for poly(vinyl chloride) alone.   When these slopes are extrapolated to zero HCl evolution, there is reasonable agreement between the measured induction time and that expected from the amount of cadmium stearate added.

Figure 2 shows the evolution of HCl from poly(vinyl chloride) solution at 190°C in the presence of three concentrations of triisodecyl phosphite. Identical steady rates are obtained in both, as with the poly(vinyl chloride) alone. However, there are induction periods before evolution of HCl commences, and the times between the parallel straight lines at a given loss of HCl (e.g., at 160 μmoles HCl $g^{-1}min^{-1}$) agree well with the expected times if the phosphite is reacting to form the phosphonate.
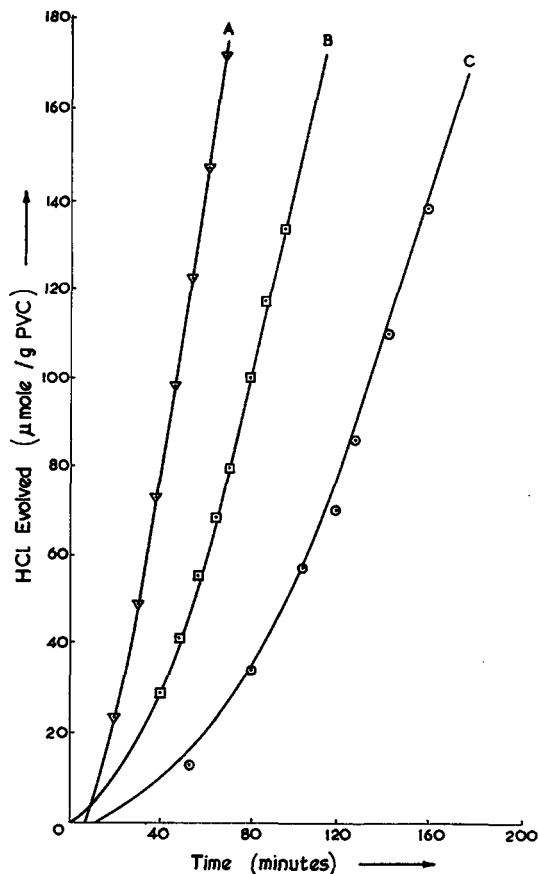

Fig. 1. Evolution of HCl from poly(vinyl chloride) heated at 190°C: (A) poly(vinyl chloride) alone; (B) plus 1.5% cadmium stearate; (C) plus 6.0% cadmium stearate.

Anhydrous hydrogen chloride was passed into triisodecyl phosphite at 180°C. An exotherm was observed, and the temperature rose to 210°C. An infrared spectrum (Perkin Elmer 237) of the liquid reaction product was compared to that of the original phosphite and showed (a) the formation of peaks at 2400 and 1260 cm^{-1} corresponding to a P—H bond and a P=O bond respectively, and (b) a change in the shape of the broad band between 900 and 1100 cm^{-1}, suggesting a change from $(RO)_3P$ to $(RO)_2P$.
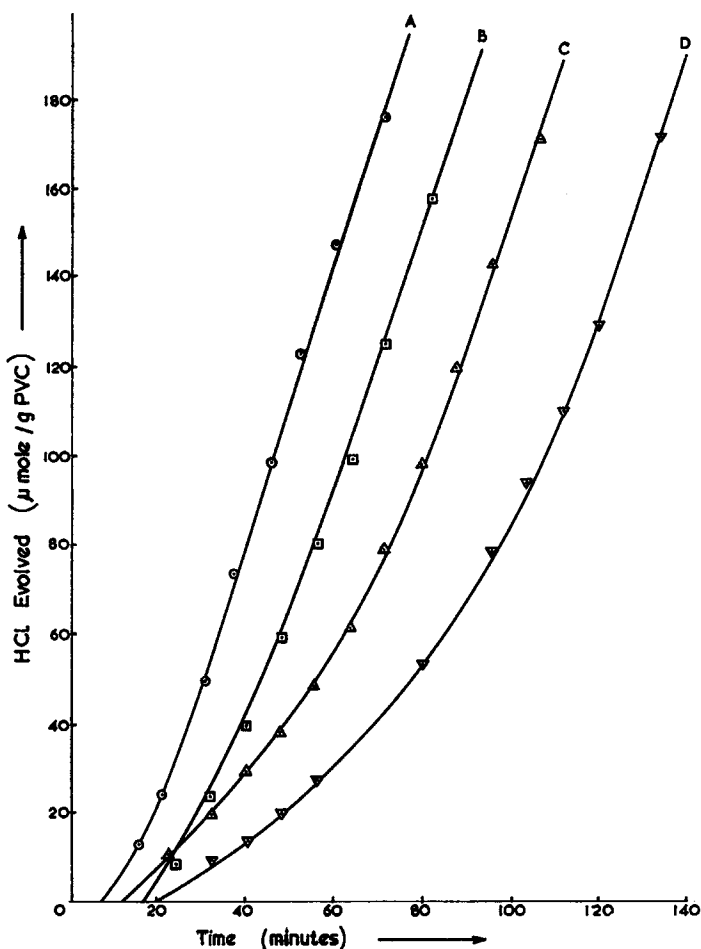
Fig. 2. Evolution of HCl from poly(vinyl chloride) heated at 190°C: (A) PVC alone; (B) with 3% triisodecyl phosphite;   (C) with 6% triisodecyl phosphite;   (D) with 11.5% triisodecyl phosphite.

In Figure 3, the evolution of HCl from solutions of poly(vinyl chloride) containing cadmium stearate and triisodecyl phosphite is shown.   It was observed that the triisodecyl phosphite improved the dispersion of cadmium stearate in the solvent and probably explains the clear induction periods in the experiment.   The steady rate of evolution of HCl is 2.0 μmoles g^{-1}-min^{-1} in both cases when the triisodecyl phosphite is present, compared with 2.3 μmoles HCl g^{-1}min^{-1} with 1.25 parts cadmium stearate alone. The separation between the extrapolation of lines A, B, and C is as expected if HCl is absorbed by the phosphite.

When the product of the reaction between the HCl and the triisodecyl phosphite was added to a solution of poly(vinyl chloride), an identical curve was obtained to that of poly(vinyl chloride) alone.   Its presence
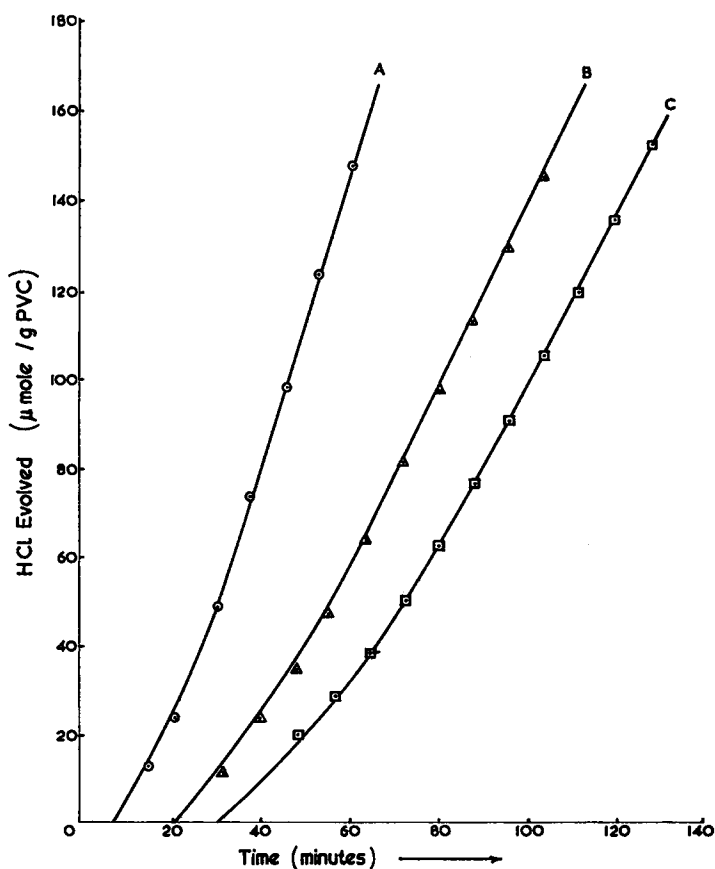
Fig. 3. Evolution of HCl from poly(vinyl chloride) with 1.25% cadmium stearate heated at 190°C: (A) PVC and cadmium stearate alone; (B) with 2% triisodecyl phosphite; (C) with 3.6% triisodecyl phosphite.

reduced the rate of degradation for poly(vinyl chloride) containing 1.25 parts of cadmium stearate in the same way as triisodecyl phosphite, but there was no induction period.

When cadmium chloride is added to the solution of poly(vinyl chloride), the evolution of HCl is increased slightly (Fig. 4). The addition of triisodecyl phosphite reduced the rate to that of PVC alone, with an induction period because of its absorption of HCl. The phosphonate also reduced the rate of degradation of PVC in the presence of cadmium chloride to that of PVC alone. The form of these curves is the same, whatever the amount of phosphonate present.

Experiments with Zinc Salts

The addition of zinc stearate has a dramatic effect on the evolution of HCl (Fig. 5). This effect can be reduced by the addition of diisodecyl phosphonate or triisodecyl phosphite, but not to the level of that for PVC alone.
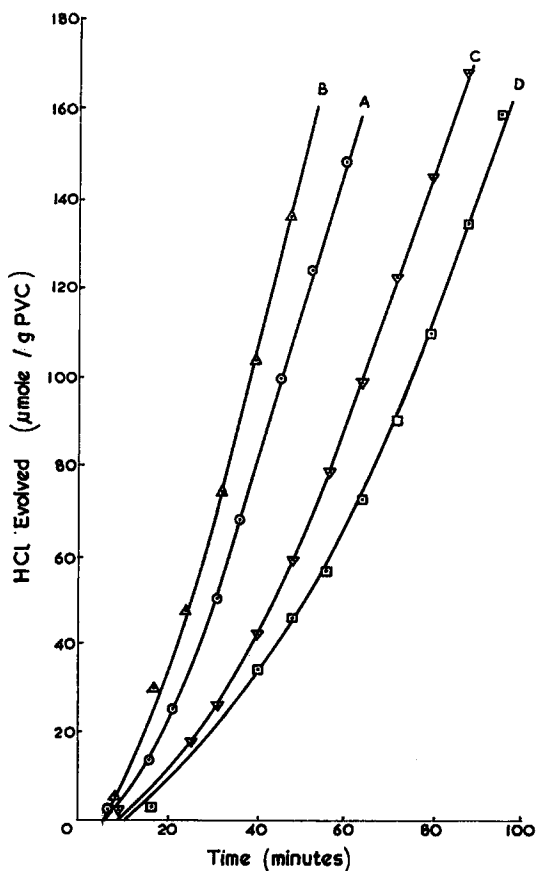
Fig. 4. Evolution of HCl from poly(vinyl chloride) heated at 190°C: (A) PVC alone; (B) with 2% cadmium chloride; (C) with 2% CdCl₂ plus 3.3% triisodecyl phosphite; (D) with 2% CdCl₂ plus 5.9% triisodecyl phosphite.

TABLE I
Rates of Dehydrochlorination of PVC with Zinc Salts
in Solution at 190°C

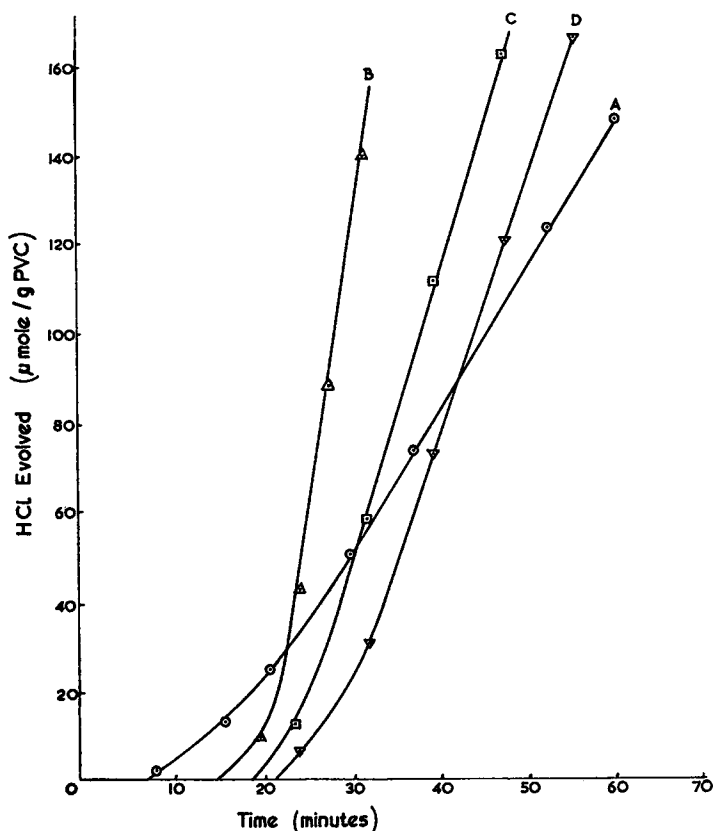| Additives, wt-% of PVC				Rate of dehydrochlorination
Zinc stearate	Zinc chloride	Triisodecyl phosphite	Diisodecyl phosphonate	μmole HCl g^{-1}min^{-1}
0	0	0	0	3
0	1.1	0	0	25.0
0	1.1	8.8	0	28.0
0	1.1	0	6.0	14.4
1.25	0	0	0	12.4
1.25	0	3.3	0	5.9
1.25	0	0	3.0	6.2

Fig. 5. Evolution of HCl from poly(vinyl chloride) heated at 190°C: (A) PVC alone; (B) with 1.25% zinc stearate; (C) with 1.25% zinc stearate plus 3.0% diisodecyl phosphonate; (D) with 1.25% zinc stearate plus 3.3% triisodecyl phosphite.

The effect of zinc chloride is even more marked (Table I). This harmful effect can be reduced by the addition of diisodecyl phosphonate but is unaffected by triisodecyl phosphite.

DISCUSSION

The addition of cadmium stearate to a solution of poly(vinyl chloride) results in a reduction in the HCl that is evolved. However, the presence of stearate does not stop HCl being formed from the polymer. The HCl formed is absorbed by the stearate. Since all the HCl is not absorbed immediately, some passes to the titration vessel. When all the stearate has been used, a constant rate of evolution of HCl is observed. As with PVC alone, this rate does not show any increase due to an autocatalytic effect because the HCl is swept from the system as soon as it is formed. However, to systems to which cadmium stearate has been added, lower steady rates of evolution of HCl have been observed. Some effect re-

mains after all of the cadmium stearate has reacted. Recently, Briggs and Wood,[9] having used a similar technique, published a study of the evolution of HCl from poly(vinyl chloride) with added laurates. They found incomplete absorption of the HCl unless synergistic mixtures of two laurates were used. We find that the simple stearates react with stoichiometric amounts of HCl early in the reaction.

When triisodecyl phosphite is added to the poly(vinyl chloride), it also reduces the HCl evolved resulting in an induction period. Briggs and Wood did not observe such an induction period. The reaction of HCl with the phosphite at 180°C proceeds exothermally and produces another liquid which infrared evidence suggests might be the phosphonate. Both the phosphite and phosphonate were observed to aid the dispersion of cadmium stearate in the PVC in di-2-ethylhexyl phthalate and hence resulted in a more rapid absorption of the HCl evolved. This might be part of the function of these compounds on technological systems, as well as reducing the deleterious effect of the metal chloride formed from the metal stearate.

Cadmium chloride added to PVC increases its rate of degradation, an increase which is reduced by the addition of either phosphite or phosphonate. The latter is thought to be the active species, possibly by chelating the cadmium ion, but is formed in situ from the reaction of phosphite with HCl.

Both zinc stearate and zinc chloride accelerate the degradation of PVC because of the catalytic action of zinc chloride. With zinc stearate, some reduction in rate can be achieved by the addition of either phosphite or phosphonate, but the rate of degradation is still higher than for the PVC alone. With zinc chloride, the increased rate is reduced by phosphonate but not by phosphite. It appears that, in this case, there is insufficient time for the phosphonate to be formed from the phosphite and affect the rate of reaction. The PVC has become gelled by the time the phosphite has been converted into phosphonate.

CONCLUSIONS

Triisodecyl phosphite reacts with HCl and would therefore be expected to prevent the autocatalytic effect of HCl on the evolution of more HCl from PVC. The reaction product, diisodecyl phosphonate, unlike the reaction product from cadmium stearate, has no action on the rate of degradation of PVC alone, but it has an effect when metal ions are present. It is proposed that phosphites are effective because phosphonates are formed which neutralize the effect of metal ions, probably by chelation.

References

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