Thermal Degradation of Poly (vinyl chloride)-Stabilization Effect of Dichlorotin Dioxine

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Thermal degradation of polyvinyl chloride (PVC) and the effect of dichlorotin dioxine (DCTD) on this process have been investigated using dehydrochlorination (DHCl) and thermogravimetric techniques. A significant decrease in the rate of degradation was observed when PVC was mixed with a small amount which was maximum with 0.25 pph of DCTD and thermal decomposition temperature with DCTD was found to be higher than that of pure PVC. The value of apparent activation energy of the dehydrochlorination process has been calculated and a suitable mechanism for the stabilizing action of DCTD on PVC has been purposed.

1. INTRODUCTION

Among the commercial polymers used, poly(vinyl chloride) (PVC) stands second in the world so far as the production is concerned. However, it is found to be thermally unstable which can reduce its useful life period considerably. Degradation of PVC has been extensively investigated [1–4] and different mechanisms have been proposed [5–12]. There are two main processes occurring in the thermal degradation of PVC. The primary process that leads to the formation

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of conjugated polyene sequence in the polymer backbone [8]. This process is, generally, believed initiated due to the presence of some inherent defects [13–15] like the presence of 1,2 dichloride structure, allylic or tertiary chlorine *etc.*, in the polymer chain. Degradation is markedly enhanced in the presence of labile chlorine and the elimination of HCl causes further unzipping reaction. The secondary process of thermal degradation leads to inter- and intra-molecular cyclization thus resulting in crosslinked structure and formation of cyclic products [16]. Various types of stabilizers are added in PVC to reduce the dehydrochlorination process. These stabilizers replace active labile substituent groups, disrupt chain reaction or inactivate the degradation products. Some of the most important stabilizers include antioxidants, metal carboxylates, organotin and antimony compounds.

Dialkyl tin carboxylates are among the most successful stabilizers [17–22] used for PVC. The organotin compounds are believed to act primarily by reacting with the labile chlorine in the polymer chain, thus inhibiting the HCl unzipping reaction. The reaction mechanism though complicated is generally believed to occur in stages. Organoboron compounds have also been used [23] to replace the allylic chlorine atoms, the major source to the instability of the polymer. In the present work, we have synthesized [24] a new aromatic tin complex and studied its effect on thermal stability of PVC. A great variety of methods such as thermal dehydrochlorination, molecular weight determination, UV-visible, IR, NMR, ESR spectroscopy, rheological measurements and TGA have been used to study thermal degradation in PVC. The dehydrochlorination technique in which the sample is subjected to isothermal heating and evolved HCl is monitored after absorption in distilled water by potentiometric, argentopotentiometric titration [25, 26] or by conductometric measurements [27–29] is considered to be a convenient and very sensitive method. The detection limit for potentiometric and argentopotentiometric titration is $10^{-2}\%$ of total HCl in the sample. In case of thermogravimetric measurements the same value equals $1.2 \times 10^{-1}\%$ for a 5 mg sample. However, in case of the conductometric method, Abbas [29] has claimed a detection limit of $10^{-4}\%$ with a conductivity meter that can measure 0.01 S in a sample of 0.1 g. In the present work, we have used dehydrochlorination coupled with conductivity measurements and

TG and DTG analyses to study the stabilizing action of tin complex on PVC.

2. EXPERIMENTAL

Thermal degradation of PVC and the effect of dichlorotin dioxine as stabilizer was studied at $180 \pm 2°C$ using DHCl. TGA and DTGA were also performed on the samples and the values of the apparent activation energy were calculated.

2.1. Chemicals

2.2.1. PVC

BDH Ltd. supplied analytical grade PVC with the following specifications was used as received.

Molecular Weight   100,000 ± 20
Viscosity number   [ISO/R 174 to 1961 (E) 87]
Particle Size   100% passes B.S. 60 mesh
                   74% passes B.S. 200 mesh

2.2.2. Tetrahydrofuran (THF)

Analytical grade peroxide free THF was obtained from E. Merck and was used as such.

2.2.3. Dichlorotin Dioxine (DCTD)

4.4 g (0.03 mol) of 8-hydroxyquinoline was taken in two necked 1-liter flask fitted with a cold water condenser, inert atmosphere, ice bath and magnetic stirrer. 150 ml of freshly distilled diethyl ether was added. 19.4 ml (0.03 ml) of *n*-butyl lithium diluted with 50 ml of diethyl ether was added drop-wise using a dropping funnel. During the addition of *n*-butyl lithium the temperature of the mixture was maintained at −20°C. The mixture was stirred overnight at room temperature during

which the yellow precipitates of lithium salt of 8-hydroxy-quinoline was formed. The precipitates were filtered under inert atmosphere, washed three times with dry ether and stored in a desiccator. DCTD was prepared by refluxing in dry methanol, tin (IV) chloride and freshly prepared lithium salt of 8-hydroxyquinoline in 1:2 molar ratios for 4 h under inert atmosphere. A yellow colored compound was filtered off, it was washed many times with methanol and dried over P_2O_5.

The complex was characterized [24] by NMR, Mößbauer, elemental analysis and IR spectroscopy.

2.2.4. Nitrogen Gas (N₂)

N_2 was used to provide dry and inert atmosphere during the sample preparation of PVC with DCTD and for conductometric measurements. It was obtained from Pak Oxygen Limited. It was purified to remove the traces of oxygen by passing it through alkaline pyrogallol solution and then dried by passing over NaOH pallets and silica gel. The purified N_2 was then passed at the rate of 20 ml/min through a reactor where PVC degradation was carried out.

2.2.5. Conductivity Water

Doubly distilled water-having conductivity in the range of $1-2$ µS was prepared in the Lab. by redistilling the water in the presence of alkaline $KMnO_4$.

For DHCl, samples (0.5 g) of pure PVC and PVC-containing 0.25 – 0.75 pph DCTD were degraded at $180 \pm 1°C$ under N_2 atmosphere having flow rate 20 ml/min. N_2 carried away the HCl produced during degradation, which was passed through a cell (diameter 4.8 cm, length 20 cm) containing 130 ml conductivity water placed in thermostat at $25 \pm 0.1°C$. Conductivity measurements were carried out using Orion Research Conductivity Meter Model 101. The detailed experimental procedure for the degradation studies has been described elsewhere [29]. Thermogravimetric and differential thermal analysis on the samples (40 mg) were carried out using Bähr Gerätebau STA 501 using Quartz crucible (diameter 0.8 cm, length 1.48 cm). The temperature

range was from 50°C to 550°C and the heating rate was 5°C/min. The carrier gas nitrogen at the rate of 10 ml/min was used.

3. RESULTS AND DISCUSSION

The elimination of HCl and the formation of polyene sequences are special characteristics of PVC degradation. This process is usually initiated at allylic chlorine sites present in the PVC chain. Once initiated the degradation process continues and zip elimination of HCl occurs with the simultaneous formation of sequences of conjugated double bonds *i.e.*, polyenes as described below;
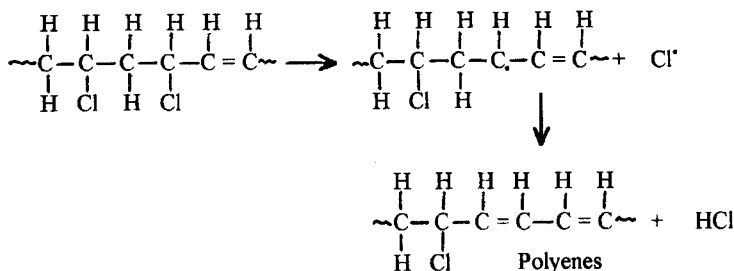
The chlorine atom that dissociates from the allylic structure attacks the same PVC molecule taking H atom from the chain to form HCl. The HCl produced as a result of degradation has been measured through conductometric measurements. Figure 1 describes the % HCl loss as function of time for PVC and PVC containing various proportions of DCTD. With pure PVC an induction period (12 min) was recorded and % HCl loss after 5 h was found to be 5.59%. When PVC was mixed with small amount of DCTD *i.e.*, 0.125 pph a small increase in the induction period was noted which increased from 12 to 18 min. However, PVC containing 0.25 pph DCTD showed the maximum induction period which was 25 min and % HCl loss after 5 h observed was 1.78%. For the samples containing 0.5 and 0.75 pph DCTD induction periods of 22 and 20 min were noticed and % HCl loss after 5 h were found to be 1.85% and 2.01% respectively which show that further increase in DCTD in PVC was not so effective in stabilizing the PVC.
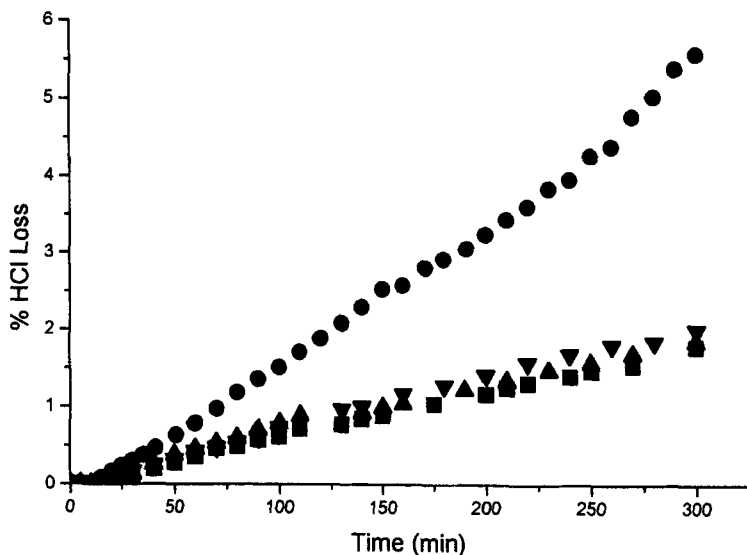
FIGURE 1   DHCl studies in the thermal degradation of PVC and PVC containing DCTD at 180°C; (●) pure PVC, PVC containing DCTD: (■) 0.25 pph, (▲) 0.5 pph, (▼) 0.75 pph.

PVC samples were also subjected to thermogravimetric analysis. Thermograms recorded by the instrument for the pure PVC and PVC mixed with 0.25–0.75 pph of DCTD are shown in Figure 2. These thermograms show two steps decomposition of the polymer. The first weight loss occurs around 270°C which corresponds to HCl evolution, while the second at about 420°C is due to the evolution of hydrocarbons. In the secondary degradation process aromatic compounds are produced through polyene decomposition.

As a result of dehydrochlorination during the first decomposition stage the linear conjugated structures may cyclized. McNeill and co-workers [30] have identified two stages of PVC degradation, during the first stage, between 200 and 360°C mainly HCl and benzene and very little alkyl aromatics or condensed ring aromatics hydrocarbons are formed. It was evaluated that 15% of the polyene generates benzene, the main part accumulating in the polymer and being active in inter-molecular and intramolecular condensation reactions by which cyclohexene and cyclohexadiene rings embedded in an aliphatic matrix are
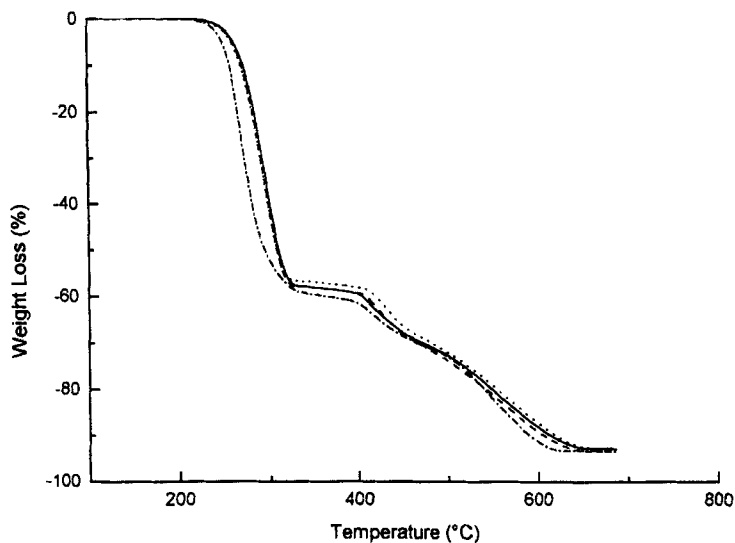
FIGURE 2   TGA curve for PVC and PVC containing DCTD; (-.-.-) pure PVC, PVC containing DCTD: (———) 0.25 pph, (-----) 0.5 pph, (......) 0.75 pph.

formed. Alkyl aromatics and condensed ring aromatics hydrocarbons are formed in the second stage [31] of degradation between 360 and 500°C, when very little HCl and benzene are formed. In this stage the polymeric network formed by polyene condensation breaks down in the process of aromatization of the above C_6 rings. The stabilization studies in PVC usually involve the first stage of degradation.

The TG curves for PVC containing complex DCTD (Fig. 2) exhibits the first weight loss at a higher temperature than the unstabilized PVC. The DTG curves were also obtained for these systems. Figure 3 indicates that unstabilized PVC has a maximum rate of degradation at 270°C where as PVC containing a very small amount of DCTD has a maximum rate of degradation at a higher temperature i.e., 296°C. These results corroborate with those obtained from dehydrochlorination method. The activation energy of the first stage of degradation in pure PVC and that mixed with DCTD were calculated using equation due to Horowitz et al. [32].

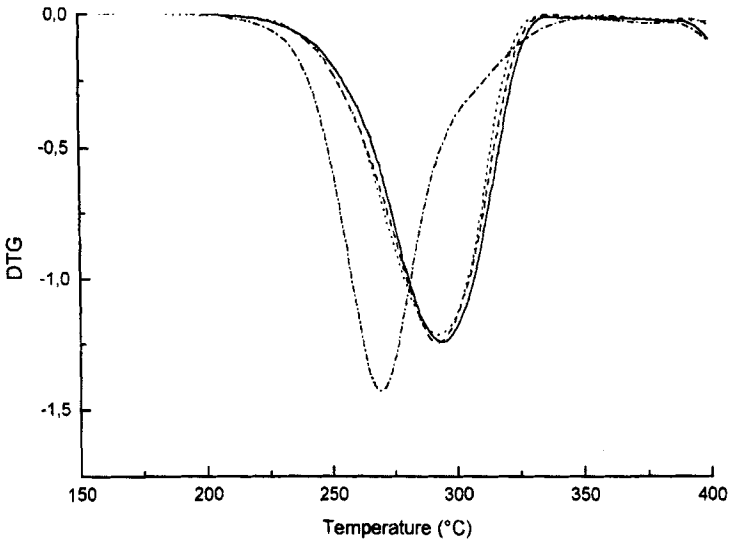$$\ln \ln \left(W_0/W \right) = E_a(T - T_s)/RT_s^2$$

FIGURE 3   DTG curves for PVC and PVC containing DCTD; (-.-.-) pure PVC, PVC containing DCTD: (———) 0.25 pph, (-----) 0.5 pph, (......) 0.75 pph.

where W_0 is the initial weight, W is the weight retained at temperature T and T_s is the inflection temperature, E_a is the apparent activation energy and R is gas constant. Figures 4–7 show the plot of ln ln (W_0/W) *vs.* $(T - T_s)$ for unstabilized and stabilized PVC systems. From the slope of these curves the apparent activation energy of the
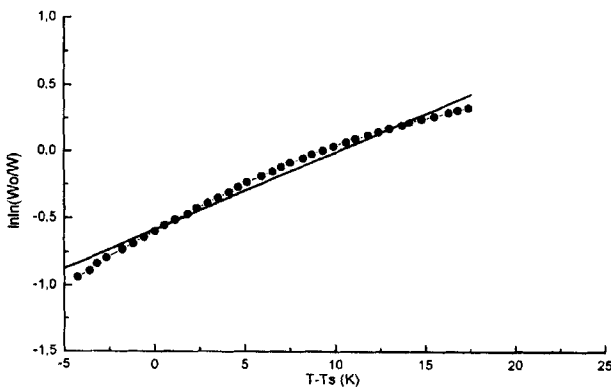

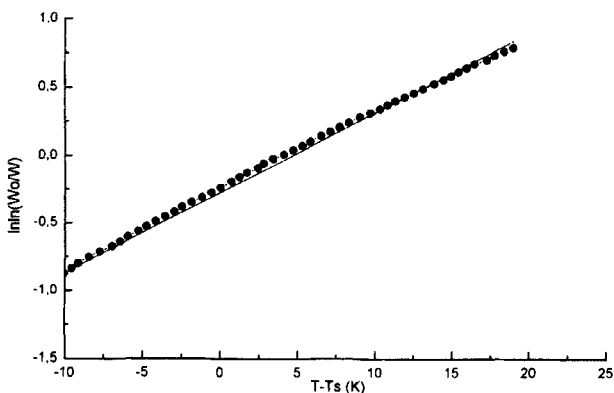FIGURE 4   Thermogravimetric analysis of pure PVC; Plot of ln ln(W_0/W) *vs.* $(T - T_s)$

FIGURE 5 Thermogravimetric analysis of PVC containing 0.25 pph DCTD; Plot of $\ln\ln(W_0/W)$ vs. $(T - T_s)$.

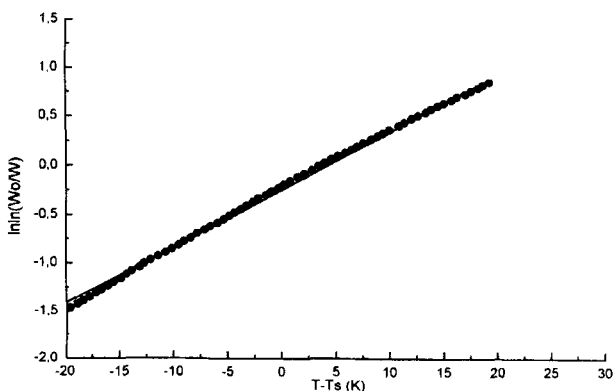

FIGURE 6 Thermogravimetric analysis of PVC containing 0.5 pph DCTD; Plot of $\ln\ln(W_0/W)$ vs. $(T - T_s)$.

process has been calculated. The values of the activation energy calculated are given in Table I.

It is clear from the Table I that the value of activation energy increases very much with small addition of the complex. However, with further addition of DCTD a small decrease in the value is noted. Thus only an optimum amount of the stabilizer is required for better results.
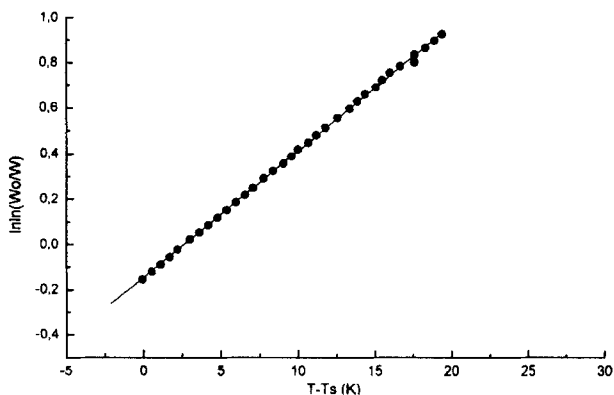
FIGURE 7   Thermogravimetric analysis of PVC containing 0.75 pph DCTD; Plot of $\ln\ln(W_0/W)$ *vs.* $(T - T_s)$.

TABLE I   Activation energies of dehydrochlorination process in PVC

	$T_s K$	$E_a kJ/mol$	%*increase*
PVC (pure)	541.4	137.7	
PVC + 0.25% DCTD	569.2	159.3	15.69
PVC + 0.5%DCTD	564.6	154.8	12.42
PVC + 0.75%DCTD	563.5	150.7	9.44

There are two reactions that can be described mainly responsible for stabilizing PVC. The exchange of labile (allylic) chlorine atom at the polymer chain for less easily removable oxine group from DCTD reduces the number of initiation sites for dehydrochlorination. The coordinate covalent bond between Sn and nitrogen breaks easily and the oxine group replaces the allylic chlorine. The bulky oxine group attached to the chain then acts as a catch or block for the unzipping reaction.
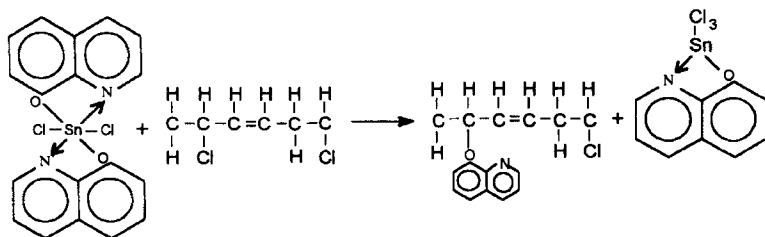
The activity of allylic chlorine is thereby reduced thus stabilizing PVC against thermal degradation. It is assumed that an optimum level of DCTD present in PVC may remove the defective structures in the polymer, a limiting stabilizing effect is thus reached. This, however, may not correspond to absolute stability of the polymer *i.e.*, the inherent instability of the normal PVC structure still exists.

The second reaction is the absorption of HCl that is produced randomly during thermal degradation of PVC. Free HCl is a polar small molecule which is very mobile ordinarily and it interact with PVC to catalyze further the degradation process in PVC by a molecular mechanism *i.e.*;
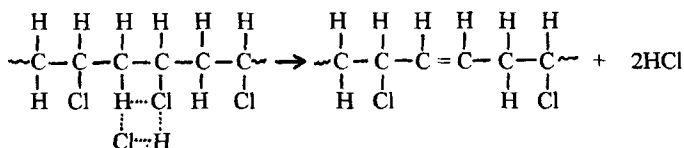
However, in the presence of DCTD, the HCl may react with the complex producing hydroxyquinoline and trichlorotinoxine. This fixation of HCl may reduce its catalytic effect but any further reaction with HCl may lead to an appreciable quantities of $SnCl_4$ which is much stronger Lewis acid and may then lead to higher degradation rate in PVC. Thus whereas a very small amount of DCTD is not sufficient enough to quench all the HCl produced an amount higher than the optimum may result in enhancement in the degradation and reduction in the value of the apparent activation energy as is evident from the TGA (Tab. I) and the dehydrochlorination studies.
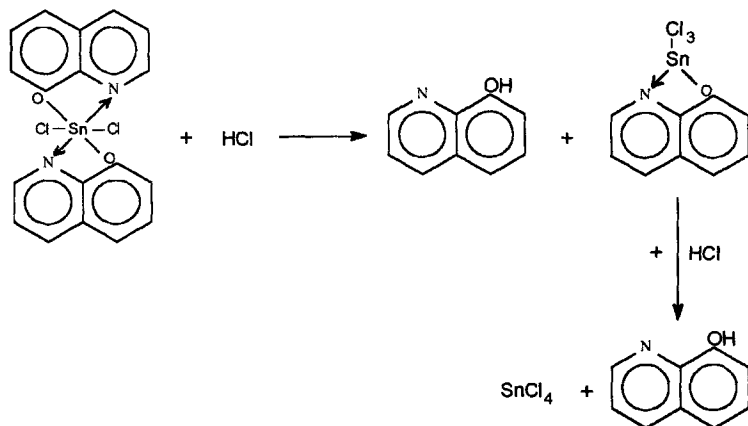
4. CONCLUSIONS

A newly synthesized organotin compound, dichlorotin dioxine was found to be a good thermal stabilizer for PVC. An optimum amount of dichlorotin dioxine, sufficient to remove the labile chlorine sites in PVC gave the best results. The values of the apparent activation energies of the dehydrochlorination process increases from 137 kJ/mol in case of pure PVC to 159 kJ/mol in the presence of 0.25 pph of this complex.

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