

## Investigation of the Photodecomposition Rate Constant of Poly (Vinyl Chloride) Films Containing Organotin (IV) Complexes

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### Abstract

The photodecomposition of poly(vinyl chloride), films containing organotin complexes (0.5% by weight) was investigated. The photodecomposition rate constant was reduced significantly in the presence of organotin complexes compared to the blank PVC. The Ph<sub>3</sub>SnL complex was found to be the most effective additive in photostabilization of PVC films. The photodecomposition rate constant for PVC films containing triphenyltin(IV) was found to be  $1.80 \times 10^{-3} \text{ sec}^{-1}$  compared to  $4.75 \times 10^{-3} \text{ sec}^{-1}$  for PVC films in the absence of any additives. [DOI: [10.22401/JUNS.20.3.04](https://doi.org/10.22401/JUNS.20.3.04)]

Keywords: Photodecomposition rate constant; Photostabilization; Organotin complexes; PVC films; Additives.

### 1. Introduction

Polymers are produced annually in huge quantities since they have various interesting industrial and medicinal applications [1–3]. Synthetic polymers are easy to produce at low cost using various convenient processes. There are 10,000 companies in the United State alone that are interested in manufacturing, processing and fabricating polymeric materials [4]. Poly(vinyl chloride) (PVC) is one of the most produced and consumed polymers worldwide [5]. It has various out door applications [6] such as construction materials [7–9]. However, long term exposure of PVC to sunlight and/or high temperature lead to its photo degradation [10]. As a result, changes in the polymer's physical and mechanical properties occur [11]. The defects or impurities within the PVC polymeric chain are the main reason for dehydrochlorination and/or photo oxidation that lead to formation of unsaturated centers [12–14]. Therefore, PVC should be protected against harsh weather conditions. Photostabilization of PVC can be established through the use of various additives. The most common additives are plasticizers [15], aromatics [16,17], heterocycles [18], Schiff base complexes [19, 20], metal complexes and inorganic salts.

Organotin complexes were used in various applications and in particular, for the stabilization of PVC [21]. In the present study,

we investigated the photodecomposition rate constant (*kd*) of PVC polymeric films containing organotin (IV) complexes on irradiation with UV light.

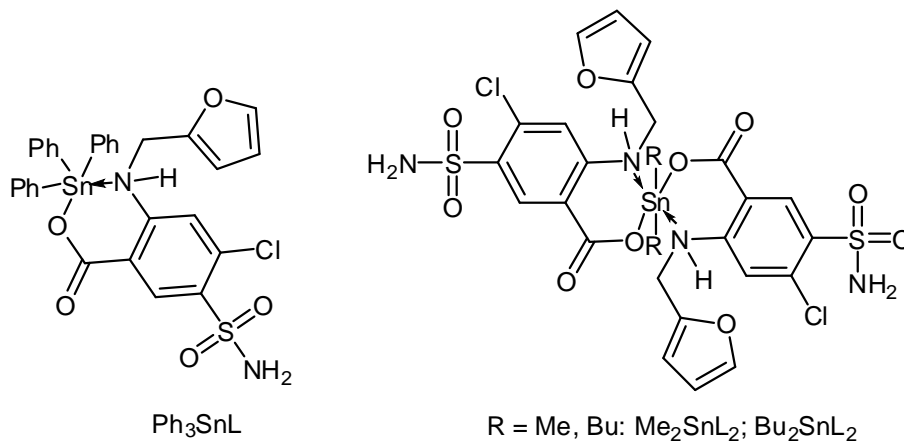
### 2. Experimental

#### 2.1. Materials

Reagents and solvents were purchased from Sigma-Aldrich (Gillingham, UK) and have been used without further purification. PVC (*K* value = 67, degree of polymerization=800) was obtained from Petkim Petrokimya (Istanbul, Turkey).

#### 2.2. Synthesis of organotin (IV) complexes

Organotin (IV) complexes Fig.(2); Ph<sub>3</sub>SnL, Me<sub>2</sub>SnL<sub>2</sub> and Bu<sub>2</sub>SnL<sub>2</sub>) were synthesised as off white powders from reactions of furosemide with chlorotriphenylstannane, dichlorodimethylstannane or dibutyldichlorostannane in methanol, based on a literature procedure [22]. The structures of Sn(IV) complexes and their purities have been confirmed by the elemental analyses and various spectroscopic data and were in agreement with the ones reported [22].



**Fig.(2): Structures of organotin(IV) complexes.**

### 2.3. Films Preparation

Commercial PVC in tetrahydrofuran (5 g/100 mL) was re-precipitated with ethanol and dried for 24 h at 20°C under reduced pressure. The organotin complexes (0.5% by weight) were mixed with PVC at 20°C and were fixed using aluminum plate stands (Q-Panel Company, Homestead, FL, USA) [23]. The thickness of PVC films (40  $\mu\text{m}$  thickness) was measured using a Digital Caliper Vernier (Kevelaer, Germany).

### 2.4. Accelerated Testing Technique

Irradiation (290–360 nm;  $\lambda_{\text{max}} = 313 \text{ nm}$ ) of PVC films was carried out using a standard procedure with an accelerated weather-meter QUV tester (Philips, Saarbrücken, Germany) [19, 20] for 300 h.

### 2.5 Photodegradation Rate ( $kd$ ) of PVC Films using UV Spectrophotometer

A Shimadzu UV-Vis 160A-Ultraviolet Spectrophotometer (Shimadzu Cooperation, Kyoto, Japan) was used to measure the changes in the UV-visible spectra of PVC films during irradiation ( $\lambda_{\text{max}} = 313 \text{ nm}$ ) [24]. The photodecomposition rate constant ( $k_d$ ) of PVC films were calculated using Equation (1).

$$\ln(a - x) = \ln a - k_d t$$

where,  $a = A_0 - A_\infty$ ,  $x = A_0 - A_t$ ,  $a$  = PVC concentration before irradiation and  $x$  = change in PVC concentration at time  $t$  during irradiation as shown in Equation (2),  $A_0$  = the absorption intensity of the PVC at  $t_0$ ,  $A_\infty$  = the absorption intensity at  $t_\infty$  and  $A_t$  = the absorption intensity after irradiation time  $t$ .

$$a - x = A_0 - A_\infty - A_0 + A_t = A_t - A_\infty$$

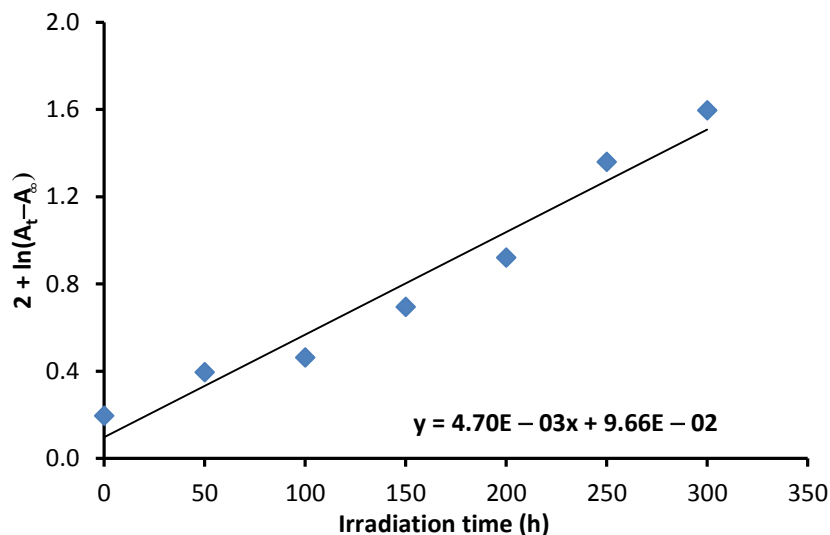
Equation (3) was obtained by substituting  $a - x$  in Equation (1) by its value in Equation (2).

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_d t$$

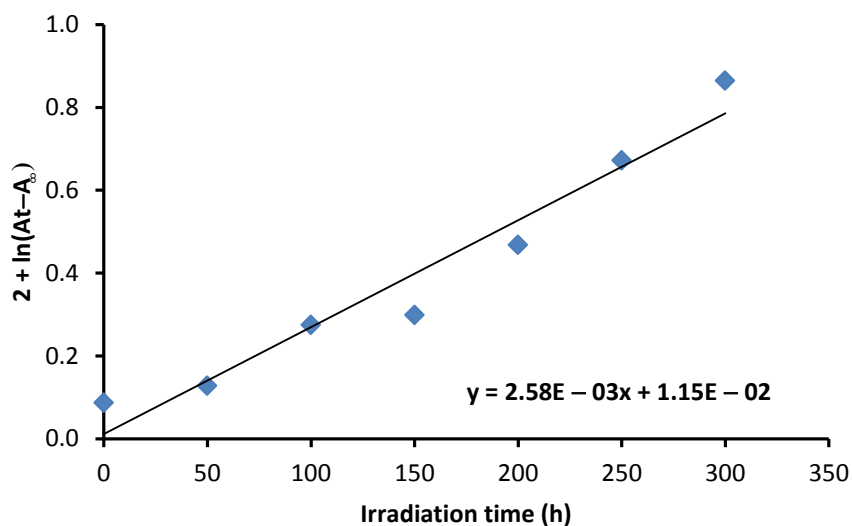
The plot of  $\ln(A_t - A_\infty)$  versus irradiation time ( $t$ ) gives straight line in which the slope equal  $k_d$ . The photodecomposition of PVC follows a first order kinetics [25].

### 3. Results and Discussion

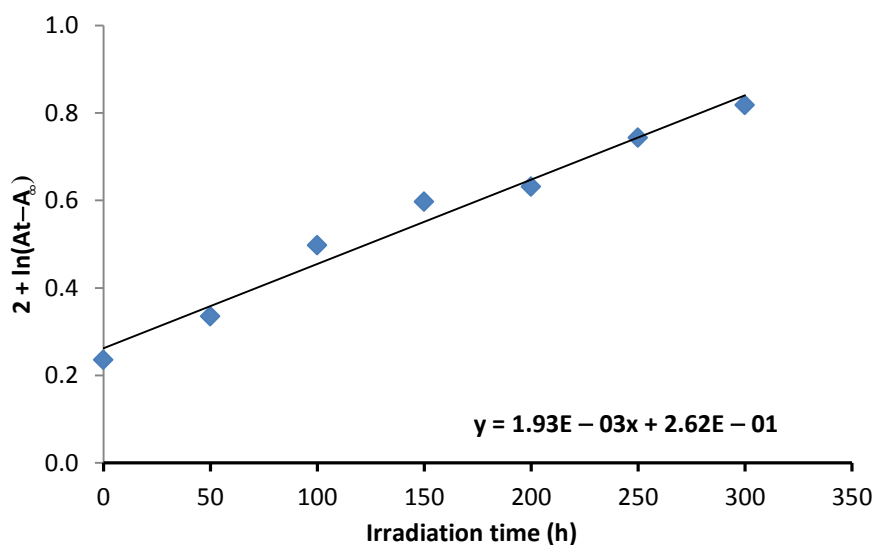
The effect of organotin (IV) complexes ( $\text{Me}_2\text{SnL}_2$ ,  $\text{Bu}_2\text{SnL}_2$  and  $\text{Ph}_3\text{SnL}$ ) on the PVC films photodecomposition was investigated. The PVC films (40  $\mu\text{m}$  thickness) containing organotin (IV) complexes (0.5% by weight) were irradiated with a UV light ( $\lambda_{\text{max}}=313 \text{ nm}$ ) for 300 h. The irradiation led to a clear change in PVC films and decomposition took place. The plot of  $\ln(A_t - A_\infty)$  against irradiation time ( $t$ ) gave a straight line. The graphs showed first order kinetics in which the slope equalled the decomposition rate constant ( $kd$ ) for PVC films. Fig.(3) shows the change in  $\ln(A_t - A_\infty)$  against irradiation time ( $t$ ) for PVC films in the absence any additives. Figures 4–6 show the changes in the  $\ln(A_t - A_\infty)$  against irradiation time for PVC films containing organotin (IV) additives (0.5% by weight) as stabilizers for PVC films on irradiation with light.



*Fig.(3): Changes in  $\ln(A_t - A_\infty)$  for PVC (blank) film with irradiation time.*



*Fig.(4): Changes in  $\ln(A_t - A_\infty)$  for PVC film containing  $Me_2SnL_2$  with irradiation time.*



*Fig.(5): Changes in  $\ln(A_t - A_\infty)$  for PVC film containing  $Bu_2SnL_2$  with irradiation time.*

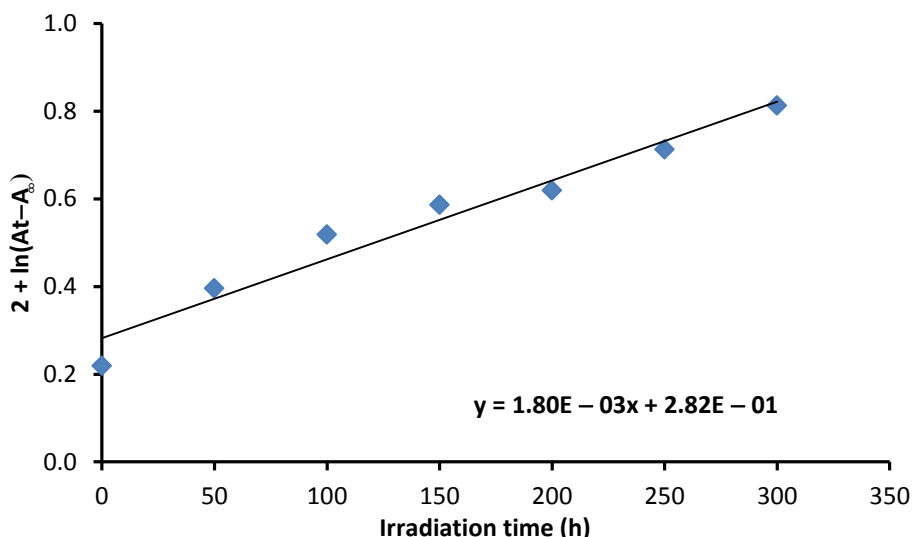


Fig.(6): Changes in  $\ln(A_t - A_\infty)$  for PVC film containing  $Ph_3SnL$  with irradiation time.

Table (1)

Photodecomposition rate constant ( $k_d$ ) for PVC films on UV irradiation (300 h).

PVC film	$K_d$ ( $sec^{-1}$ )
PVC (blank)	$4.70 \times 10^{-3}$
PVC + $Me_2SnL_2$	$2.58 \times 10^{-3}$
PVC + $Bu_2SnL_2$	$1.93 \times 10^{-3}$
PVC + $Ph_3SnL$	$1.80 \times 10^{-3}$

The first order photodecomposition rate constant ( $k_d$ ) for PVC films containing organotin (IV) complexes (0.5 wt %) along with that for PVC (blank) is shown in Table (1). Table (1) and Figs. (3–6) show that the rate constant ( $k_d$ ) values are sensitive to the presence of organotin (IV) complex and its type. The PVC photodecomposition rate constant for PVC films was high ( $4.70 \times 10^{-3} sec^{-1}$ ) in the absence of any additives. Such rate constant has been reduced significantly ( $1.80$ – $2.58 \times 10^{-3} sec^{-1}$ ) when organotin (IV) complexes were used as additives. The photostabilization of PVC in the presence of organotin (IV) complexes follow the order of  $Ph_3SnL > Bu_2SnL_2 > Me_2SnL_2$ . The triphenyl (IV) complex was the most efficient than the other organotin complexes in photostabilization of PVC films presumably due to the resonance of the extra phenyl group (*i.e.* acted as a better radical scavenger) [22].

Clearly, organotin (IV) complexes have acted as photostabilizers for the

photostabilization of PVC films. The photodecomposition rate constant was highest for PVC (blank) and lowest in the presence of triphenyltin (IV) complex. Such photostabilizers could act as HCl scavengers, peroxide decomposers, primary stabilizers, UV absorbers and radical scavengers [26–28].

#### 4. Conclusions

The photodecomposition rate constants for PVC films containing organotin (IV) complexes have been reduced significantly compared to the PVC in the absence of any additives. The photodecomposition rate constant for PVC films containing organotin (IV) was  $1.80$ – $2.58 \times 10^{-3} sec^{-1}$  compared to  $4.75 \times 10^{-3} sec^{-1}$  for the blank PVC film. Triphenyltin (IV) complex was the most effective complex towards the photostabilization of PVC. Such complex can be used as a PVC photostabilizer for long term protection from sunlight and/or UV radiation.

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