

UV-photoassisted degradation of phenyltin(IV) chlorides in water

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Abstract

The UV degradation of triphenyltin (TPT), diphenyltin (DPT) and monophenyltin (MPT) chlorides in water was studied. The UV-photoassisted degradation of TPT in water takes place by sequential dephenylation via DPT and MPT. Results are also presented concerning the photodegradation of TPT and DPT in different atmospheric gases. The chemical nature of the surrounding atmosphere seems to affect the photodegradation rate of the TPT species, but not that of DPT. © 1997 Elsevier Science S.A.

Keywords: Photodegradation; Phenyltins; Environment

1. Introduction

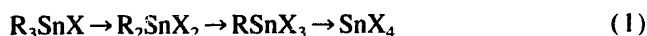
During the last decades, interest in many countries in the environmental chemistry of organotin compounds has risen dramatically, and several articles have been written [1,2] reporting either general or particular aspects of this topic. The reason for the increased awareness of the environmental aspects of organotins is due primarily to the wide range of industrial applications discovered for organotin chemicals. In fact, tin has a larger number of organometallic derivatives in commercial use than any other element [3].

Triphenyltin (TPT) compounds have been widely used [4] to combat a range of fungal diseases in various crops. They also possess antifeedant properties and, additionally, may act as insect chemosterilants [5]. The use of marine paints [6] containing tributyltin (TBT) and to a lesser extent triphenyltin (TPT) compounds, as toxic additives, has been found to be very effective in eliminating this problem.

Besides the wide range of industrial applications of organotin compounds, the toxicological pattern of organotin chemicals is well known. Thus, although inorganic tin compounds are basically not harmful, some organotin species, as TBT and TPT, are toxic to both animal and vegetable life. This has resulted in regulations restricting their use in EU countries.

Several studies [7–9] of the fate of organotins have emphasized the disappearance of the compounds, either after application to crops or on exposure to ultraviolet light.

The degradation of an organotin compound is defined as a progressive removal of the organic group from the tin atom as follows:



(where R and X are organic and inorganic radicals, respectively).

This stepwise loss of organic groups is accompanied by a progressive decrease in toxicity [2]. The UV fraction of sunlight reaching the Earth's surface is one of the main factors responsible for organotin compound degradation in the environment.

In a previous paper [10], the UV photolytic degradation of butyltin species in water was reported. The aim of the present work is to provide data on the mode of UV degradation of triphenyltin compounds in water and to identify some of the breakdown products.

2. Experimental details

2.1. Materials

TPT chloride (95%), diphenyltin (DPT) dichloride (96%) and monophenyltin (MPT) trichloride (98%) were supplied by Aldrich. The concentrations of the compounds studied ($1 \mu\text{g ml}^{-1}$) were chosen by considering their solubilities in water [2]. The gases used in the experiment (N_2 , He) were supplied by SEO-ALPHAGAZ and their purity was better than 99.998%.

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2.2. Methods

The photochemical experiments were performed using a Hanovia photochemical reactor (1 l). A medium pressure mercury lamp (100 W), fitted with a synthetic high purity quartz envelope, was used as a light source. The light passed through a space between two thimbles in which cooling water was circulating. The UV emission from the lamp includes energy at 185, 238, 248, 254, 265, 280, 297, 300, 313 and 366 nm. The incident radiant flux reaching the reactor per unit surface was measured using a radiometer (LICOR, Inc. model LI-188B; sensor, LI-190SB). Taking into account the lamp spectral distribution indicated by the manufacturer, we calculated the photon flux absorbable by the phenyltin species to be approximately 3.2×10^{20} photons s^{-1} in the UV region of $\lambda < 300$ nm.

UV-visible absorption spectra were recorded on a Perkin-Elmer 554 spectrophotometer equipped with 1.0 cm quartz cells.

Analysis of TPT and the other phenyltins was performed on a Perkin-Elmer 8410 gas chromatograph equipped with a flame photometric detector (610 nm filter) and a glass (SPB-1) semicapillary column (15 m \times 0.53 mm ID) using helium as move phase. The chromatographic parameters were optimized previously [11]. Other aspects concerning the analytical procedure can be found elsewhere [11].

Inorganic tin(IV) was analysed on a Perkin-Elmer 2380 atomic absorption spectrometer equipped with an HGA-300 graphite furnace.

3. Results and discussion

3.1. Kinetic aspects

Fig. 1 shows the UV-visible absorption spectra of the phenyltin chlorides in aqueous solutions in systems open to the air. As can be seen, the absorptions are below 290 nm.

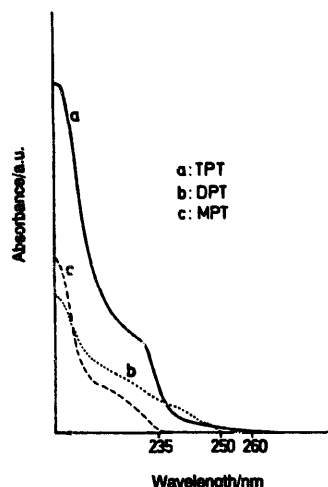


Fig. 1. UV absorption spectra of (a) TPTCl, (b) DPTCl₂, (c) MPTCl₃, in water at pH 5.5–6.0.

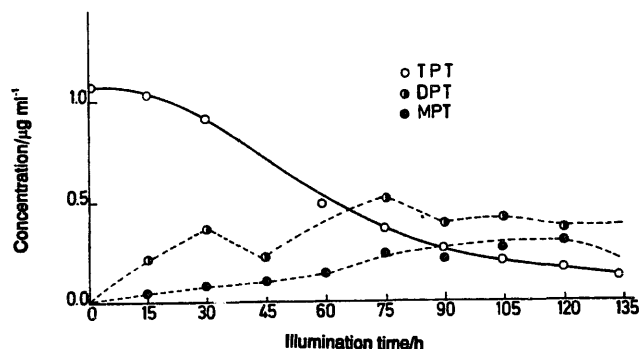


Fig. 2. Kinetic profiles of the variation in concentration of species detected during the UV-photodegradation of TPTCl in water (pH 5.5–6.0) at ambient temperature and in an air-equilibrated atmosphere.

Thus, as in the case of butyltin compounds [10], illumination in the 190–290 nm region can initiate photoprocesses in these phenyltin compounds. The Sn–C bond may be ruptured photochemically, since the dissociation energies of Sn–C bonds are [12] in the range 190–220 kJ mol^{-1} and UV light of wavelength 290 nm has an energy of approximately 411 kJ mol^{-1} .

Fig. 2 shows kinetic profiles of the variations in concentration for the degradation of the TPT derivative in water under an atmosphere open to the air with UV stimulation. It also shows the time-course of the products generated in this process: DPT and MPT.

From the results shown in Fig. 2, it can be deduced that the disappearance of the TPT species under UV light is accompanied by a simultaneous increase in the concentration of the DPT and MPT species in the medium during the photoprocess. Atomic absorption analysis did not detect the presence of any inorganic tin possibly generated in the medium. This may be because of the low initial concentration of TPT (around 1 $\mu g\ l^{-1}$). These results suggest that, as in the case of TBT [10], the nature of TPT photodegradation is typical of a sequential dephenylation process, as indicated in Eq. (1).

From the same figure, it can be seen that both the DPT and MPT species accumulate in the medium with increasing illumination time, and their concentrations increase progressively and in an almost parallel manner. This implies that the rates of degradation of TPT to DPT and DPT to MPT are very close. The balance of material (the sum $[TPT] + [DPT] + [MPT]$) during the 120 min of illumination is practically constant, remaining around 1 $\mu g\ l^{-1}$. This seems to indicate a certain resistance to inorganic tin in dephenylation processes, so that inorganic tin does not appear in a detectable amount in the medium, at least before 120 min and below its limit of detection by atomic absorption. Nevertheless, the presence of inorganic tin in very low concentration in the medium cannot be ruled out.

Soderquist and Crosby [13], studying TPT degradation in water under the stimulus of solar or UV light, found that TPT is degraded by homolytic rupture of the Sn–C bond to Ph_2SnO , and did not find Ph_4Sn , MPT or inorganic tin as

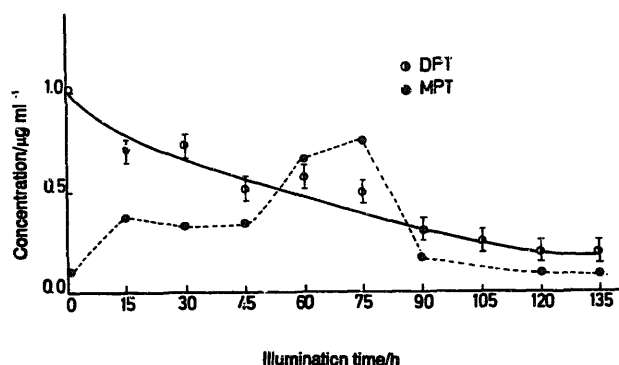


Fig. 3. Kinetic profiles of the variation in concentration of species detected during the UV-photodegradation of DPTCl_2 in water (pH 5.5–6.0) at ambient temperature and in an air-equilibrated atmosphere.

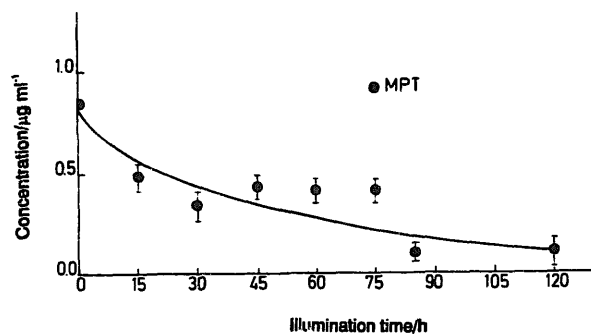


Fig. 4. Kinetic profiles of the variation in concentration of species detected during the UV-photodegradation of MPTCl_3 in water (pH 5.5–6.0) at ambient temperature and in an air-equilibrated atmosphere.

products. However, a water-soluble organotin polymer $(\text{PhSnO}_x\text{H}_y)_n$ was detected, leading to the conclusion that this polymer is the final product of TPT photodegradation in water. A previous work [14] had concluded that the triphenyltin derivative Ph_3SnOAc is photodegraded to inorganic tin by a dephenylation sequence via DPT and MPT. Our results also indicate that TPT photodegradation seems to occur by a sequential dephenylation process, with DPT and MPT species being detected in the medium, as shown above. The non-detection of inorganic tin under our conditions could be related to the formation of the organotin polymer observed by Sordesquist and Crosby [13], although—as mentioned above—it could be that inorganic tin was not detected because of its low concentration in the medium.

UV photodegradation of the two DPT and MPT species in water has also been studied separately and under identical experimental conditions to those of TPT photodegradation [10]. Figs. 3 and 4 show the results of the photodegradation of DPT and MPT respectively. As can be seen, the initial concentration of DPT (approximately $1 \mu\text{g l}^{-1}$) fell to $0.2 \mu\text{g l}^{-1}$ after about 135 min of illumination (Fig. 3) and that of MPT to $0.1 \mu\text{g l}^{-1}$ in 120 min (Fig. 4). Under the same conditions and after an illumination time of 135 min, $1 \mu\text{g l}^{-1}$ of TPT was degraded to a concentration of $0.1 \mu\text{g l}^{-1}$.

Kinetic analysis of the results of the photodegradation of the TPT, DPT and MPT species, shown in Figs. 2–4 respectively, is given in Table 1, together with quantum yields (QYs), studied in the following section. The values of the observed rate constant, $k(\text{obs.})$, were calculated in accordance with pseudo-first-order kinetics for the three individual phenyltin species (Fig. 5).

As can be seen, under UV light the rate constants of the three species are very similar. That of DPT is relatively low, suggesting the rate-determining step of progressive photodegradation of TPT to inorganic tin to be the photodephenylation of DPT to MPT.

3.2. Quantum yields

Estimated quantum yields for the photodegradation of the phenyltin species (results shown in Figs. 2–4) are given in Table 1. These values are the quantum yields estimated from the different UV-visible absorptions shown in Fig. 1 for the three phenyltin derivatives. TPT shows absorption from 265 nm, DPT from 250 nm, and MPT from 235 nm (Fig. 1). Consequently, for each compound the light absorbed was estimated from the lamp's photon flow for each emission line below the respective absorption value for the species. As can be seen, the values of quantum yield indicate a UV-stimulated dephenylation sequence for phenyltin derivatives similar to that observed by us in the case of debutylation [10] and by Blunden [15] in the UV-photoassisted dealkylation of methyltin compounds in water.

3.3. Effect of the surrounding atmosphere

In the series of butyltin derivatives, the nature of the surrounding atmosphere affected their rate of photodegradation

Table 1
Physicochemical parameters and intermediate products generated in the photodegradation of phenyltin chlorides in water

Phenyltin species	$k(\text{obs.}) \times 10^2 (\text{h}^{-1})$	Atmosphere	Intermediate products ^a	QY $\times 10^6$
TPTCl	106.3	Air	Phenol (major product)	1.12
	127.8	Nitrogen	2,3,4-Trichlorophenol ^b 2,4,5-Trichlorophenol ^c	—
DPTCl ₂	68.7	Air	—	3.73
	65.6	Nitrogen	—	—
MPTCl ₃	101.9	Air	—	12.96

^a After 135 min of illumination under the indicated atmosphere.

^b Retention time 34:43. Molecular ion m/z 196.

^c Retention time 34:54. Molecular ion m/z 196.

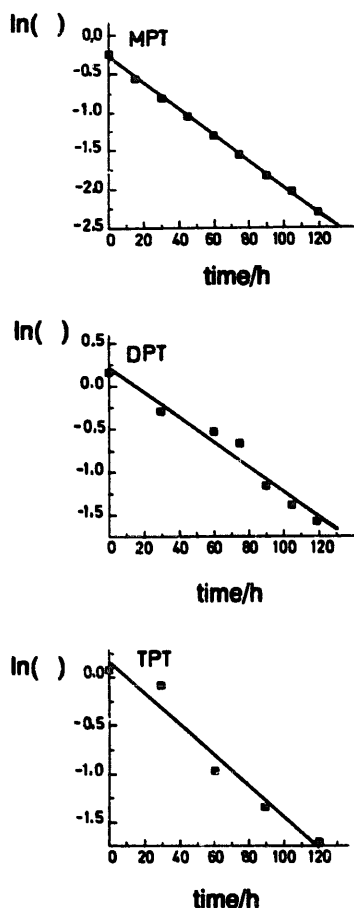


Fig. 5. Graph of kinetic study of the processes of degradation of the species indicated, from the results shown in Figs. 2 and 3. The results fit well with pseudo-first-order kinetics (logarithm of concentration vs. time).

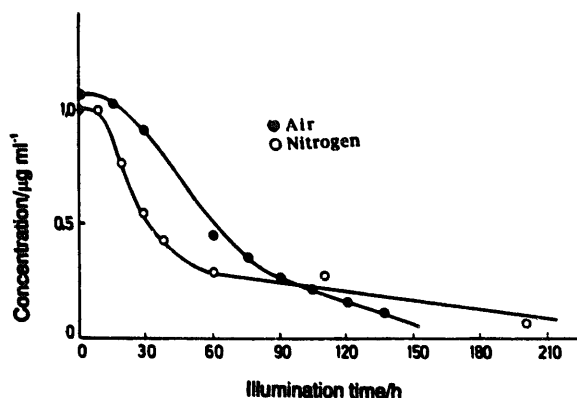


Fig. 6. Effect of the chemical nature of the surrounding atmosphere on the photodegradation of TPTCl.

[10]. This effect has also been studied in the case of phenyltin compounds.

Fig. 6 summarizes the results of independent experiments in which around $1 \mu\text{g l}^{-1}$ of the TPT species was illuminated under different atmospheres: nitrogen and air. As the figure shows, the presence of molecular oxygen plays a negative role in TPT photodegradation. However, an inert atmosphere such as molecular nitrogen seems to help the photodegradation of this species. In the case of the DPT derivative, the behaviour is different (Fig. 7). The photodegradation rate of

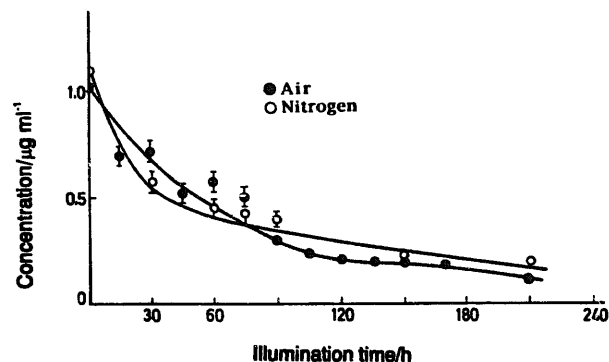


Fig. 7. Effect of the chemical nature of the surrounding atmosphere on the photodegradation of DPTCl₂.

this species seems to be practically independent of the chemical nature of the surrounding atmosphere, whether it be air or nitrogen.

As can be seen in Table 1, the value of $k(\text{obs.})$ for the TPT species is slightly higher when the photodegradation was carried out under nitrogen than when open to the air, while the $k(\text{obs.})$ values for DPT are similar under the two indicated atmospheres. These quantitative data are in accordance with the degradation profiles of the two species under different atmospheres (Figs. 6 and 7).

The results, in conjunction with those obtained in equivalent studies of butyltin species [10], seem to indicate the important role played not only by the surrounding atmosphere but also by the R group (alkyl or aryl) united with the tin atom in the photodegradation of organotins.

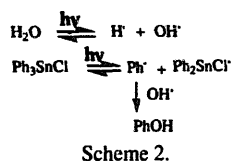
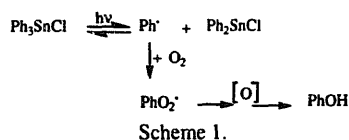
In the case of the TPT derivative, the role of oxygen in photodegradation could be explained with the same arguments used for the case of the TBT compound [10]: a deactivating effect on the singlet or triplet excited state by molecular oxygen present in the medium. However, again, this hypothesis cannot be used to explain the results for DTP (Fig. 7), as there seems to be no appreciable effect.

3.4. Analysis of products

Some of the products identified by GC–MS analysis in the liquid phase after photochemical degradation of the TPT species illuminated for 135 min under two different atmospheres are discussed below.

One of the major products found in the photodegradation of the TPT species under atmosphere open to the air was phenol, resulting from oxidation. However, phenol was not found as a product of TPT photodegradation under nitrogen atmosphere, although polychlorophenols were, some of which are given in Table 1. In all cases, the starting products and other tin derivatives were found as traces after 135 min of illumination.

When the experiments are performed under an atmosphere open to the air, the molecular oxygen present can react with the phenyl radical formed by photolysis of the Sn–C bond, as indicated in Scheme 1.



Under nitrogen, however, the phenol derivative could be formed by the OH radicals photogenerated from water [16] (Scheme 2).

The presence of chlorophenols could be attributed to photolytic rupture of the Sn–Cl bond, since it has a dissociation energy of 154 kJ mol^{-1} [17] and light of wavelength 290 nm has an energy of 411 kJ mol^{-1} . Once the Cl^\cdot radical is formed, this can attack the benzene ring of the phenol.

In the photolytic degradation of TPT under an oxygenated atmosphere, no chloro-derivatives appear as partial oxidation products. This does not indicate they have not been formed, as they could be present in very low amounts, given that the initial levels of TPT were around $1 \mu\text{g l}^{-1}$. However, in the photolytic degradation of TPT under a nitrogen atmosphere, such chloro-derivatives appear as partial oxidation products. The explanation proposed here is that there could have been a reaction of the Cl^\cdot radicals with the molecular oxygen dissolved in the medium. In fact, Cl^\cdot radicals can react with molecular oxygen dissolved in the medium, since the formation of chlorine dioxide and oxyhalogen radicals is very well known [18]. However, the formation and participation of the Cl/ClO species in the present-day atmosphere is also known [16].

4. Conclusions

The UV-photoassisted degradation of triphenyltin(IV) chloride in water takes place via sequential dephenylation.

The quantum yields of the photodegradation of phenyltin(IV) species increased with decreasing number of phenyl groups united with the tin atom. The phenyltin species offer high resistance to photodegradation, given that the quantum yields were as low as 10^{-6} .

GC–MS analysis of the photoassisted degradation of triphenyltin(IV) chlorides under atmospheres of molecular nitrogen or air, up to 135 min of illumination, shows peaks attributable to the photogenerated intermediate products present in the liquid phase. In an atmosphere open to the air, the major product was phenol, while under molecular nitrogen, the major products found were chloro-phenols.

Finally, the presence or absence of molecular oxygen seems to affect the photodegradation rate of the TPT species, although not that of DPT.

Acknowledgements

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