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Received for review March 19, 1979. Accepted September 13, 1979.

Degradation of Triphenyltin Hydroxide in Water

Charles J. Soderquist[1] and Donald G. Crosby*

The behavior of triphenyltin hydroxide (Ph_3SnOH) in dilute aqueous solution has been examined. The solubility in water was 1.2 mg/L at pH 7–9 and 6.6 mg/L at pH 4.2. Solutions at pH 5–10 were stable in the dark even at 32 °C and did not lose Ph_3SnOH by volatilization. However, aqueous Ph_3SnOH was readily degraded by homolytic cleavage of the tin–carbon bond to diphenyltin oxide when exposed to sunlight or to UV light in a laboratory photoreactor, and the photolysis rate was markedly increased in the presence of acetone. While neither tetraphenyltin, monophenyltin species, nor inorganic tin were detected as products, the formation of a water-soluble, nonextractable organotin polymer was indicated. A similar product distribution was observed for the decomposition of aqueous diphenyl- and monophenyltin species, even in the absence of light.

Triphenyltin hydroxide (Ph_3SnOH, Du-Ter) belongs to the organotin class of agricultural chemicals which includes tricyclohexyltin hydroxide (Plictran) and triphenyltin acetate (Ph_3SnOAc, Brestan). Du-Ter is currently under investigation in California as a fungicide for use on rice. As part of a study of the fate of chemicals used in rice culture (Soderquist and Crosby, 1975; Soderquist et al., 1977), we are investigating the environmental chemistry of Ph_3SnOH.

The widespread use of Ph_3SnOAc in Europe has resulted in a number of reports on its degradation in the environment (Cardarelli, 1977). While Ph_3SnOAc and Ph_3SnOH are chemically very similar, extrapolation from these previous studies is limited since they were conducted on substances such as soil and leaf surfaces, while rice culture involves application of Ph_3SnOH directly to the water in the flooded field. Using radiolabeled materials, earlier workers generally concluded that Ph_3SnOAc degrades through di- and monophenyltins to inorganic tin—a terminal product of no toxicological significance (Evans, 1974). Our study began with development of procedures suitable to routine analysis for these potential degradation products in water without need for radiolabels (Soderquist and Crosby, 1978).

The purpose of the work reported here was to examine the environmental fate of Ph_3SnOH in dilute aqueous solution, including aqueous solubility, aqueous reactivity (hydrolysis reactions), volatilization rate from water, and the effects of sunlight (photodegradation).

Department of Environmental Toxicology, University of California, Davis, Davis, California 95616.
[1]Present address: California Analytical Laboratories, Sacramento, CA 95814.

For brevity, each of the phenyltin species is referred to here as though it existed only in cationic form (e.g., Ph_2Sn^{2+}); this formalism is not meant to imply exact identities for these species in dilute aqueous solution.

EXPERIMENTAL SECTION

Reagents. Dichloromethane and hexane were nanograde or equivalent and carbon disulfide and diethyl ether were analytical reagent grade (Mallinckrodt). Water was distilled and passed through Amberlite XAD-4 resin (Rohm and Haas) unless otherwise specified; the resin was purified as described elsewhere (Woodrow and Seiber, 1978). All other chemicals were used as received. Buffered solutions employed the Carmody system, with final concentrations in the following ranges: boric acid, 2–0.2 mM; citric acid, 0.5–0.05 mM; trisodium phosphate, 1–0.1 mM. All glassware was cleaned by soaking in 2 M hydrochloric acid followed by copious rinses with distilled water.

Standard Tin Compounds. Organotin chromatographic and fortification standards were prepared at the milligram/milliliter level in dichloromethane (DCM) with Ph_3Sn^+ [as either triphenyltin chloride or triphenyltin hydroxide (Alpha Ventron)]; Ph_2Sn^{2+} as diphenyltin dichloride (Research Chem. Corp.) or diphenyltin oxide (Thompson–Hayward, dissolved in DCM/acetic acid, 95:5); $PhSn^{3+}$ as phenyltin trichloride (Research Chem. Corp.); and Ph_4Sn (Aldrich). Du-Ter (Thompson–Hayward), a wettable-power formulation containing 47.5% Ph_3SnOH, was used as received. An inorganic tin standard was prepared by dissolving 0.250 g of tin metal in 150 mL of concentrated hydrochloric acid and diluting to 0.50 L; further dilutions were made with a 5% sulfuric acid/2.5% citric acid (w/v) mixture. Uniformly ring-labeled ^{14}C diphenyltin dichloride was provided by Thompson–Hayward. Each of the standard compounds was judged to be

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Table I. Responses of Tin Compounds to PCV Spray Reagent[a]

compd	1 μg	10 μg
Ph_4Sn	−	−
Ph_3SnOH	−	−
Ph_3SnCl	−	+
$(Ph_3Sn)_2O$	−	+
Ph_2SnCl_2	++	++
$PhSnCl_3$	++	++
$(Bu_3Sn)_2O$	−	−
Bu_2SnCl_2	++	++
$BuSnCl_3$	++	++
Na_2SnO_3	++	++
Sn^{4+} (in HCl)	++	++
Sn^{4+} (in NaOH)	+	+

[a] Strong blue (++), weak blue (+), no blue (−) for compounds spotted on TLC and observed 5 min after spraying with PCV.

of 95% or greater purity by thin-layer chromatography (TLC), except $PhSnCl_3$ which contained 10–20% Ph_2SnCl_2 (it was not purified).

Methods. *Analysis.* Water samples were analyzed for Ph_3Sn^+, Ph_2Sn^{2+}, $PhSn^{3+}$, Ph_4Sn, and inorganic tin (Sn^{4+} plus SnO_2) by the method of Soderquist and Crosby (1978) unless otherwise specified. Briefly, the method consists of DCM extraction of an acetate-buffered water sample, concentration of the extract under nitrogen, and conversion of the phenyltins to their volatile hydrides with lithium aluminum hydride. The derivatives were separated and quantitated by electron-capture gas–liquid chromatography (EC–GLC). Values reported are not corrected for percent recovery (60–90%).

Benzene, toluene, biphenyl, and phenol were isolated from 100-mL water samples by extraction and then detected by flame-ionization gas–liquid chromatography (FID–GLC) utilizing a Varian Model 2400 equipped with either a 5 m × 2 mm (i.d.) stainless steel column packed with 10% DC-200 on 60/80 mesh Gas-Chrom Q or a 0.6 m × 2 mm (i.d.) glass column packed with 3% OV-17 on 68/80 mesh Gas-Chrom Q; injector and detector temperatures were 275 °C, and the carrier gas (nitrogen) flow rate was 20 mL/min. Benzene and toluene were determined by extraction with 5 mL of carbon disulfide, followed by analysis of the extract without concentration on the DC-200 column at 110 °C; recovery of each was greater than 80% with a sensitivity of about 0.05 mg/L (the carbon disulfide contained about 1 mg/L of benzene as an impurity). Biphenyl was determined by extraction with 10 mL of hexane, concentration of the extract under nitrogen, and analysis on the OV-17 column at 125 °C; recoveries exceeded 80%, and the method was sensitive to 0.007 mg/L. Phenol was determined by extraction with three 10-mL portions of diethyl ether after acidification of the water to pH 3 or less with hydrochloric acid and the combined extracts were concentrated under nitrogen and analyzed with the OV-17 column at 70 °C; recoveries averaged 64%, and the method was sensitive to 0.05 mg/L.

TLC was carried out on precoated 20 × 20 cm, 0.25 mm thick silica gel 60 F-254 plates (Brinkman) developed one to three times in benzene–acetic acid–methanol (88:4:8 by volume). Visualization was by fluorescence quenching or by spraying with a 1% aqueous solution of pyrocatechol violet (PCV) (Eastman Organic Chemicals) containing 1% cetyltrimethyl-ammonium bromide (Aldrich); responses of the pertinent compounds to the visualization spray are given in Table I.

Ultraviolet and visible spectra were obtained with a Cary Model 15 spectrometer. Liquid-scintillation counting (LSC) was performed with a Packard Model 2425 utilizing 7a70B scintillation cocktail (RPI Corp.). Radioactive spots on TLC plates were located with a Berthold Series 6000 thin layer scanner.

Aqueous Solutions. The aqueous solutions of organotin compounds for hydrolysis, volatilization, and photodegradation studies were prepared in two ways. Where the presence of extraneous chemicals was intolerable, solutions were prepared as in the solubility studies (see below), usually filtered through a fine porosity (4–5 μm) glass filter and diluted with an additional 10% volume of water before use (the "saturation" method). Alternately, when the presence of organic solvents was less important or when rapid preparation of solutions was called for, the organotins were added in a small (0.1–1.0 mL) volume of carrier solvent (usually methanol) to a rapidly stirred water sample (the "solvent" method).

Solubility. The solubility of Ph_3Sn^+ was determined by the method of Haque and Schmedding (1975) with a 9.0-L glass carboy coated inside with 40 mg of Ph_3SnOH and filled with unbuffered water (pH 6.5). When a number of solutions were to be monitored concurrently, smaller containers were used: Ph_3SnOH (10 mg) dissolved in 10 mL of diethyl ether was added to a 1.0-L horizontal glass bottle, and the bottle was rotated gently until all the ether had evaporated to leave a uniform coating of Ph_3SnOH on the walls. After removal of the last traces of ether with nitrogen, the bottle was carefully filled with buffer and slowly stirred with a Teflon stir bar in the dark at ambient temperature. Samples (100 mL) were transferred from the center of the bottle after 3 days (or the carboy after 8 days) by aspiration and the concentration of Ph_3Sn^+ determined in duplicate both with and without prior filtration through a 4–5 μm glass filter.

Hydrolysis. The aqueous stabilities of Ph_3Sn^+, Ph_2Sn^{2+}, and $PhSn^{3+}$ were examined by addition (solvent method) of the phenyltin to 3.0 L of water until the solution was homogeneous (usually about 1 h). The resulting solution was divided equally among three flasks, adjusted to the appropriate pH with Carmody buffer (Table II), sealed, and maintained in the dark. Duplicate 50-mL samples were removed at intervals and analyzed for the appropriate phenyltin.

Volatilization. The rate of volatilization of Ph_3Sn^+ from

Table II. Hydrolysis of Phenyltins

Ph_3Sn^+ remaining, mg/L								Ph_2Sn^{2+} remaining, mg/L			
21 °C				32 °C				21 °C			
	pH				pH				pH		
days	4.6	6.9	10.0	days	4.2	7.1	9.8	days	5.5	7.0	8.5
0	0.38	0.39	0.39	0	0.44	0.44	0.46	0	0.19	0.20	0.21
2	0.38	0.31	0.41	14	0.37	0.40	0.39	0.4	0.18	0.20	0.19
7	0.38	0.33	0.39	29	0.36	0.39	0.38	1.0	0.15	0.17	0.18
13	0.31	0.37	0.38					2.1	0.082	0.11	0.11
20	0.28	0.36	0.42					4.0	0.049	0.065	0.11
30	0.32	0.40	0.43					6.3	0.032	0.033	0.066

Table III. Nonextractable Material from Aqueous [^{14}C]Ph_2Sn^{2+}

days	percent of total found		total as % of theory[a]
	nonextract.	extract.[b]	
0	4.7	95.3	93.3
1	13.5	86.5	90.0
4	30.1	69.9	82.9
6	39.5	60.5	70.5
12	52.9	47.1	70.8

[a] 1.2×10^7 cpm (170 μg of Ph_2Sn^{2+} of 90–95% purity) in 1.0 L of pH 7.0 buffered water in the dark at 22 °C. [b] Ph_2Sn^{2+} partitions 97.3% into DCM with 2.7% remaining in the aqueous phase under these conditions.

dilute aqueous solution was measured with a 1.0 mg/L solution (solvent method) at pH 8.2 (unbuffered). Identical 600-mL beakers providing a surface of 54 cm^2 were filled with 500 mL of solution, held at 32° in a constant temperature bath, and monitored as described previously (Soderquist et al., 1977).

Photolysis. Photodegradation experiments were carried out either indoors with light sources which closely simulated the effects of sunlight (Crosby and Tang, 1969) or outdoors in sealed borosilicate glass flasks under ambient conditions. Temperatures in the indoor photoreactors were 25–30 °C, while those outdoors often reached 40 °C during summer in Davis, CA. In a typical experiment, 3.5 L of pH 7.2 (unbuffered) water containing about 1 mg/L of Ph_3Sn^+ (saturation method) was divided between a laboratory photoreactor, a sealed flask placed outdoors in November sunlight, and a flask held in the dark as a control. Samples (200 mL) were withdrawn at intervals, acidified with two drops of concentrated sulfuric acid, and stored at 5 °C until analyzed.

Polymer Identification. Carbon-14 labeled Ph_2Sn^{2+} (170 μg, 1.2×10^7 cpm) was added to 1 L of pH 7.0 (buffered) water and the solution held in the dark at 22 °C. Samples (10 mL) were withdrawn periodically and extracted with two 5-mL portions of DCM in the presence of acetate, and aliquots of the resulting aqueous and organic phases were assayed by LSC for non-extractable and extractable activity, respectively (Table III). After 12 days, 100-mL samples were extracted with DCM to remove all traces of Ph_2Sn^{2+}, placed briefly under vacuum to remove dissolved solvent, and treated with Amberlite XAD-4 resin according to the procedure of Steelink (1977). The resin was eluted with various solvents, e.g., acetone, methanol/acetic acid, 3 M hydrochloric acid, or aqueous sodium hydroxide (0.01–1.0 M). Analysis was by LSC throughout the procedure.

Nonlabeled phenyltin trichloride (100 mg) was added to 1 L of water and adjusted to pH 7.0 with sodium hydroxide causing a cloudy mixture which remained unsettled for days. After 6 days, a 100-mL portion was filtered through Whatman 42 paper (the residue accounted for the bulk of added chemical and yielded a single spot on TLC at the R_f of $PhSn^{3+}$) and the filtrate extracted with DCM. The resulting aqueous phase was concentrated at 40 °C under vacuum and treated with XAD-4 resin as before. The resin was then rinsed with water until neutral to litmus and eluted by stirring with 0.5 M potassium hydroxide for 1.5 h. Analysis was by the usual colorimetric method throughout the procedure.

RESULTS AND DISCUSSION

Solubility. Our main purpose here was to obtain a value which reflected true solution, but not necessarily the maximum solubility, of Ph_3Sn^+. The methods of Haque and Schmedding (1975) and Biggar and Riggs (1974) both met this criterion; the former was the simplest and was used. Filtering through a fine porosity (4–5 μm) glass filter assured that particles inadvertently dislodged from the container walls would not distort the analysis. The results (Table IV) indicate an increased solubility at lower pH, and the agreement between unbuffered and buffered solutions at comparable pH shows that increased solubility due to complexing by buffer components was negligible. Experiments which follow were generally begun at or below a concentration of 1.0 mg/L. The solubility of Ph_3Sn^+ should be independent of counterion when bonding is primarily ionic (e.g., chloride, bromide, acetate); each should exchange with hydroxide and yield free triphenyltin cation (Neumann, 1970). While there are no previous reports on the solubility of Ph_3SnOH, Barnes et al. (1973) give a value of 3.3 mg/L for Ph_3SnOAc at unspecified pH, and Meyling and Pitchford (1966) obtained values for Ph_3SnOAc comparable to ours at similar pH.

Table IV. Solubility of Triphenyltin Hydroxide

pH	Ph_3Sn^+ found, mg/L	
	filtered	unfiltered
6.5[a]	0.78	1.1
4.2	6.6	7.9
7.0	1.2	1.2
8.7	1.3	1.3

[a] For the 9-L unbuffered sample; other data are for the buffered 1-L samples.

Attempts to measure the solubility of Ph_2Sn^{2+} and $PhSn^{3+}$ were precluded by their instability in water. While both should be more soluble than Ph_3Sn^+ at low pH, their ability to form insoluble oxides or hydroxides at neutral and basic pH predicts solubilities lower than those of Ph_3Sn^+ under environmental conditions.

Hydrolysis. In the context of our study, hydrolysis encompasses all reactions of tin species with water. Since the phenyltin chlorides become aquated (hydroxylated at neutral to basic pH) almost instantaneously (Poller, 1970), we were primarily concerned with water-mediated C–Sn bond cleavage. Ph_3Sn^+ was stable in water even after 30 days at 32 °C (Table II). Ph_2Sn^{2+}, however, was rapidly hydrolyzed at all pH values, with a half-life of 2–3 days (Table II). After about 2 months, each of the resulting Ph_2Sn^{2+} solutions yielded only about 0.02 mg/L of inorganic tin and TLC showed Ph_2Sn^{2+} and $PhSn^{3+}$ to be barely detectable in the pH 8.5 sample while absent in the other two. That the lack of identifiable products was not due to wall adsorption was shown when a similar aqueous solution containing [^{14}C]Ph_2Sn^{2+} buffered at pH 5.2 retained more than 90% of its radioactivity over a 7-day period. The small loss occurred within the initial 0.5 day and was slowly reversed when the solution was made strongly basic.

Examination of the stability of $PhSn^{3+}$ in water proved more difficult. As previously described (Soderquist and Crosby, 1978), the determination of aqueous $PhSn^{3+}$ was precluded by very rapid loss even upon fortification directly into a separatory funnel containing acetate-buffered water and DCM extractant. As the conversion of $PhSn^{3+}$ to the hydride ($PhSnH_3$) proceeded quantitatively during analysis whether the substrate was added as $PhSnCl_3$ or $PhSnO_2H$, it appeared that formation of some other product was occurring during the fortification step. Numerous attempts to account for the $PhSn^{3+}$, such as by analysis for benzene, phenol, and biphenyl as degradation products, and analysis of the DCM extract for $PhSn^{3+}$ by either the hydride or the nonspecific organotin procedure, all allowed no recovery (6% $PhSn^{3+}$). Furthermore, while

Table V. Photolysis of Triphenyltin Hydroxide in Water

conditions	irradiation, days	species found, mg of Sn/L: Ph_3Sn^+	Ph_2Sn^{2+}	$PhSn^{3+}$	Ph_4Sn	total extractable tin	Sn^{4+} plus SnO_2	total: mg/L[a]	total: % of[b] day zero
photoreactor	3	0.22	0.023	0.014	<0.002	0.30	0.012	0.31	100
	7	0.22	0.036	<0.005	<0.002	0.23	0.012	0.24	77
	14	0.11	0.028	0.030	<0.002	0.16	0.013	0.17	55
	21	0.085	0.015	<0.005	<0.002	0.12	<0.010	0.12	39
	36	0.024	0.007		<0.002		<0.010		
natural sunlight	3	0.29	0.017	0.030	<0.002	0.25	<0.010	0.25	81
	7	0.33	0.027	<0.005	<0.002	0.27	<0.010	0.27	87
	14	0.22	0.029	0.019	<0.002	0.21	0.011	0.22	71
	21	0.13	0.021	<0.005	<0.002	0.18	0.011	0.19	61
	36	0.088	0.013		<0.002		<0.010		
limit of detectability		0.005	0.005	0.005	0.002	0.015	0.010	0.010	

[a] Total extractable tin, Sn^{4+}, and SnO_2 analyses. [b] Day zero Ph_3Sn^+ 0.92 mg/L, equivalent to 0.31 mg/L of tin.

analysis of the resulting aqueous solution showed some tin IV cation and slightly more tin IV oxide, the total accountability for $PhSn^{3+}$ was still less than 10%. Fortification of water samples with $PhSn^{3+}$ at high levels (4 mg/L) allowed 81–89% recovery by the nonspecific organotin procedure, even with a 10 h interval before analysis. Thus, while relatively large amounts of $PhSn^{3+}$ in water could be accounted for, concentrations more appropriate to the environment (0.1 mg/L or less) resulted in substantial loss. Freitag and Bock (1974) likewise encountered difficulty in the extraction of $PhSn^{3+}$ via its solvent-soluble complex with tropolone or sodium diethyldithiocarbamate. While no recovery data were reported, only small amounts of $PhSn^{3+}$ was removed from treated sugar beet leaves; most remained unextracted and was referred to as "hydrolyzed or aged $C_6H_5Sn^{3+}$ and Sn^{4+}".

Volatilization. Ph_3SnOH did not volatilize from water even though the high temperature (32 °C) caused water loss at a rate of 55 ± 3 mL/day. The Ph_3Sn^+ concentration during 6 days averaged at 0.88 ± 0.13 mg/L in marked contrast to other compounds for which the same procedure had been used to measure volatilization (Soderquist et al., 1977). While the lack of volatilization of Ph_2Sn^{2+} and $PhSn^{3+}$ was not examined, consideration of their physical properties suggests that they should not partition from water to the atmosphere. The potentially volatile halide or acetate derivatives rapidly form cations or hydroxides in water; these are nonvolatile, as are their corresponding high-molecular-weight (polymeric) oxides.

Photodegradation. Laboratory photolysis experiments aimed at predicting environmental transformations should satisfy four criteria. First, only artificial light sources with wavelengths more than 290 nm (e.g., the commercially available F40BL fluorescent UV lamps) should be used; they allow accurate prediction of product distributions found from actual field studies (Soderquist et al., 1977). Second, the matrix in which the chemical is to be irradiated should match as closely as possible that expected in the environment. The use of Ph_3SnOH in rice culture where water is the predominant matrix is, of course, what lead us to examine the aqueous chemistry of the phenyltins. Third, the initial substrate concentration should be as low as is practical in order to minimize artificial bimolecular reactions. Finally, the potential role of sensitizers should be taken into consideration.

Previously reported photochemical studies with Ph_3SnCl and Ph_3SnOAc did not adequately meet these criteria. While Chapman and Price (1972) correctly avoided 254-nm light in one set of experiments, their matrix consisted of Ph_3SnOAc coated on a glass plate. Barnes et al. (1973) irradiated Ph_3SnOAc on silica gel with 254-nm light.

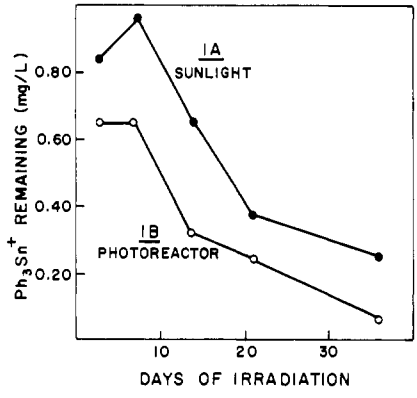

Figure 1. Photolysis of triphenyltin hydroxide in pure water. See Table III for products.

Freitag and Bock (1974) utilized sugar beet leaves but added the $Ph_3{}^{113}SnCl$ with an unspecified emulsifier, did not report a dark control, and concluded that degradation proceeded by loss of benzene because heated aqueous suspensions of Ph_3SnCl produced that substance. These studies all reported breakdown of Ph_3Sn^+ through Ph_2Sn^{2+}, $PhSn^{3+}$, and Sn^{4+} and led to acceptance of a simple sequential loss of phenyl groups as the environmental photodegradation mechanism. No photochemical work on Ph_3SnOH has been reported previously.

While the UV absorption spectrum of Ph_3SnOH shows a maximum at 257 nm (ϵ = 900, methanol), there is still some absorption in the sunlight region of the spectrum (ϵ = 5 at 290 nm); Ph_3Sn^+ might therefore be expected to undergo photolysis when exposed to sunlight. Indeed, aqueous solutions held outdoors or in the laboratory photoreactor (Figure 1) exhibited photochemical degradation. Analysis indicated the presence of small amounts of Ph_2Sn^{2+} and tin IV oxide, low and variable amounts of $PhSn^{3+}$, and no detectable Ph_4Sn (Table V). Analysis of the final (36 day) extracts and the extracted aqueous phases by TLC revealed no other compounds which quenched fluorescence or responded to PCV spray. Likewise, the profiles resulting from FID–GLC analysis of the concentrated extracts indicated no additional products. The dark control retained a constant level of Ph_3Sn^+ (0.31 ± 0.05 mg of Sn/L), and no other analytes were detectable. When the photoreactor was drained, rinsed with water and DCM, and soaked with 1.0 M sulfuric acid for 1 week, the acid rinse contained 84 μg of tin, equivalent to about 0.065 mg of Sn/L in the original solution.

The effect of pH on the photolysis of Ph_3Sn^+ was examined by irradiating pH 4.2 and 8.7 solutions outdoors

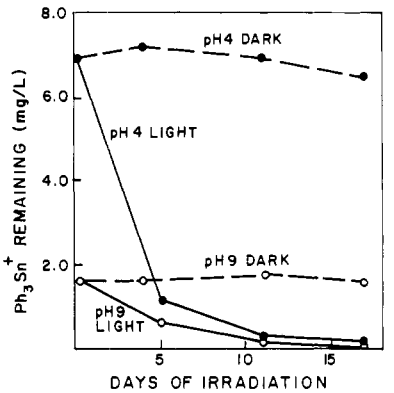

Figure 2. Photolysis of triphenyltin hydroxide in water at pH 4 and 9.

Table VI. Photolysis of Du-Ter in Water

days of irrad.	species found, mg of Sn/L			total as % of added[a]
	Ph_3Sn^+	Ph_2Sn^{2+}	Sn^{4+}	
24	0.15	0.018	0.081	37
55	0.042	0.003	0.023	10
95	0.006	<0.001	0.046	8

[a] 0.68 mg of Sn/L added as Du-Ter formulation.

in June sunlight (Figure 2). Photolysis seemed to proceed slightly more rapidly under basic conditions, and both pH extremes showed more rapid loss than the neutral (pH 7.2) photolysis described earlier (Figure 1); this may be only an indication of the difference in sunlight intensity between June and November and illustrates one advantage (constant intensity) of the F40BL photoreactor.

Outdoor irradiation of Du-Ter (40 mg in 9 L of water) was conducted in June; analysis for Ph_3Sn^+ and Ph_2Sn^{2+} indicated nearly complete photodegradation (Table VI). Neither a DCM/acetic acid (95:5) rinse nor a subsequent 2 M hydrochloric acid rinse released from the walls any material responsive to the usual colorimetric procedure for tin. However, fusion of the container bottom with potassium hydrogen sulfate yielded a substantial amount of tin (0.76 mg or 12% of the original level). While this fusion procedure was originally designed to account for tin IV oxide, other materials which would be solubilized only by alkali fusion could also have been present. Lack of tin in the preceding rinses rules out adsorption of intact phenyltins or inorganic tin IV.

The role of sensitizers was examined by simultaneous exposure to the following series of samples outdoors (each was initially at 0.50 mg of Ph_3Sn^+/L, solvent method): (a) water, (b) filtered rice-field water, (c) 2% aqueous acetone, and (d) 50 mg/L of rose bengal; identical samples were retained indoors as dark controls (they remained unchanged). The results (Figure 3) show that both acetone and rose bengal strongly promote the photodegradation of Ph_3Sn^+. Contrary to previous studies on certain chemicals which are either stable or only slowly degraded in sunlight (Soderquist et al., 1977; Ross and Crosby, 1973), natural water did not increase the photolysis rate in this case. In an additional experiment, 4 L each of purified water and filtered rice field water were fortified with Ph_3Sn^+ at 1.0 mg/L (solvent method) and exposed outdoors (July) for 50 days. Again, decomposition rates in the two water types were nearly identical as were the levels of Ph_2Sn^{2+} detected at the indicated sampling times.

The low levels of Ph_2Sn^{2+} detected in the photodegradation experiments indicated that it, too, must undergo degradation at a rate comparable to that of Ph_3Sn^+. This was confirmed when separate 0.50 mg/L solutions of

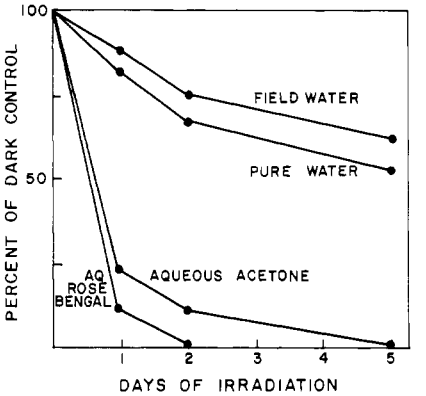

Figure 3. Photolysis of triphenyltin hydroxide in the presence of photosensitizers.

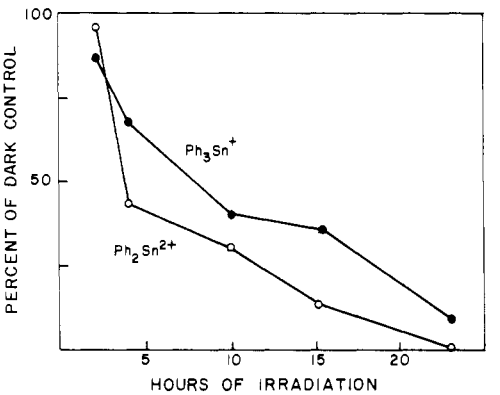

Figure 4. Comparison of photolysis rates of triphenyltin and diphenyltin in 5% aqueous acetone.

Ph_3Sn^+ and Ph_2Sn^{2+} in 5% aqueous acetone were exposed to outdoor sunlight (Figure 4). Since dilute aqueous solutions of Ph_2Sn^{2+} held in the dark were also unstable (Table II), the extent of photodegradation is difficult to assess.

Attempts to determine the fate of the phenyl group lost during such photolysis experiments failed due to the low starting levels of Ph_3Sn^+ and the long duration of the study. However, when a more concentrated solution of Ph_3Sn^+ (20 mg/L) in 5% aqueous acetone was irradiated outdoors for 13 h until 2.6 mg/L of Ph_3Sn^+ remained, 2.4 mg/L of benzene and a small amount of biphenyl (0.035 mg/L) were produced and were absent from controls. Toluene, which could have arisen by combination of phenyl radicals with methyl radicals generated from the photolysis of acetone, and phenol were both absent. Benzene and phenol were stable to sunlight under the experimental conditions. The source of hydrogen abstractable by phenyl radicals for benzene production probably was acetone, although photoreductions of this type previously have been observed even in distilled water (Crosby and Wong, 1973). While extrapolation of results of photolysis in aqueous acetone to true environmental conditions is questionable, this approach has been recommended (EPA, 1975) and in this case served to both increase the solubility of Ph_3Sn^+ while shortening the time required for significant photolysis to occur. It is anticipated that photodegradation of Ph_3Sn^+ in natural water containing organic solutes, such as in a rice field, also would yield benzene as a product.

The formation of benzene and biphenyl during photolysis in aqueous acetone is consistent with a mechanism involving homolytic cleavage of the C–Sn bond to yield phenyl radical and a hydroxydiphenyltin radical (I) (Figure 5). I could abstract hydrogen from its surroundings to yield II, but considering the known instability of tin hy-

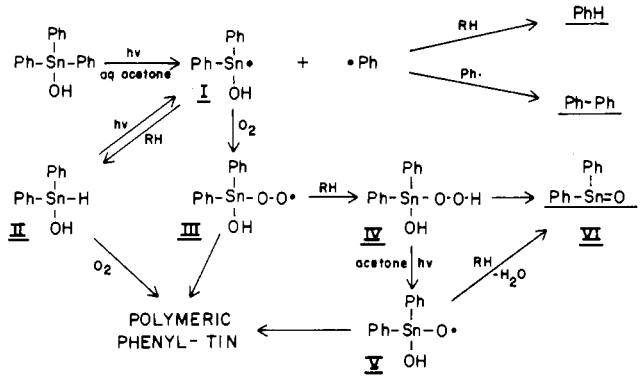

Figure 5. Proposed degradation pathway for the photolysis of Ph_3Sn^+ in aqueous acetone.

drides to light (Ingham et al., 1960), II should immediately revert back to I. Dissolved oxygen, initially present in greater than 25 M excess over Ph_3Sn^+, is known to react rapidly with organotin radicals (Brilkina and Shushunov, 1969) and should provide the hydroperoxide IV via the peroxy radical III. The confirmed product VI (diphenyltin oxide) could result either from rearrangement, for which there is precedent with analogous carbon compounds (Brown et al., 1955), or from acetone-sensitized cleavage of the peroxide bond (Walling and Gibian, 1965) through V followed by hydrogen abstraction. If the loss of Ph_3Sn^+ were accompanied by complete conversion to benzene (and an inorganic tin species), about 11 mg/L of benzene would be expected; the 2.4 mg/L found represents slightly less than one-third of this level, suggesting that further degradation of Ph_2Sn^{2+} by homolysis does not occur. Ph_2Sn^{2+} does disappear rapidly in light in the presence of acetone (Figure 4) and more slowly in the dark (Table II).

The photolysis experiments showed that aqueous Ph_3Sn^+ photodegraded in natural and simulated sunlight, that the process was promoted by acetone, that a radical mechanism appeared to be involved in the formation of Ph_2Sn^{2+}, and that analysis for those products predicted by sequential loss of phenyl groups (Ph_2Sn^{2+}, $PhSn^{3+}$, and Sn^{4+}) plus consideration of adsorption of species on the container walls was insufficient to give an adequate mass balance.

Polymer Formation. The poor recoveries of $PhSn^{3+}$ during analysis (Soderquist and Crosby, 1978), the aqueous instability of Ph_2Sn^{2+} and $PhSn^{3+}$, and the lack of identifiable products after prolonged photolysis may be reflections of the same phenomenon. We suggest that the apparent loss of extractable tin species is due to formation of a phenyltin polymer, which is water-soluble and nonextractable and perhaps generated through a monophenyltin species:

$$Ph_2Sn^{2+}(aq) \xrightarrow{\text{slow}} [PhSn^{3+}(aq)] \xrightarrow{\text{fast}} (PhSnO_xH_y)_z(aq) \quad (1)$$

While the literature reveals no previous examples of this behavior for aryltins, similar reactions of lower monoalkyltins have been investigated in some detail (Clark and Puddephatt, 1972), as illustrated by

$$EtSnOSnEt \xrightarrow{\text{pH 5}} [EtSnO_2H]_n \xrightarrow[\text{(slow)}]{\text{base}} EtSnO_2^- \quad (2)$$

They also reported a butyltin cyclic trimer and other $BuSnO_2H$ polymers of unknown structure with molecular weights of 1800–4000. Dialkyltins are also believed to form dimers based on a four-membered ring (Alleston et al., 1961) and methyltin trichloride was reported to form a hydroxychloride in water which, upon dilution, yielded an undefined (polymeric?) substance (van den Berghe and van der Kelen, 1965). Additional examples of polymeric structures are given in Neumann (1970). The formation of simple dimers or trimers appears to be less likely in our case since they would be expected to be extractable from aqueous solution and would have appeared in the nonspecific organotin analysis.

To determine whether a polymeric phenyltin could be formed, two experiments were carried out. In the first, an aqueous solution of $[^{14}C]Ph_2Sn^{2+}$ held in the dark showed a decreasing proportion of extractable radioactivity with time (Table III). The DCM-extractable radioactivity was shown by TLC to be solely Ph_2Sn^{2+}, indicating conversion of Ph_2Sn^{2+} to a water-soluble, nonextractable material. Activity was retained (>90%) when the aqueous phase was concentrated at 40 °C under vacuum, after DCM extraction at pH 1.0–10.5, and after DCM extraction preceded by acid digestion (3 M sulfuric acid at 100 °C for 15 min). TLC showed that the aqueous radioactivity remained at the origin while $PhSn^{3+}$ exhibited an R_f of 0.05. About 60% of the radioactivity was removed by XAD-4 resin, and 40% of this was recovered by an elution with 1.0 M sodium hydroxide; elution with other solvents was not successful. These results are consistent with the behavior of polymeric humic and fulvic acids, for which the XAD-4 resin procedure was designed (Steelink, 1977).

Since the radiolabeled study could not provide sufficient material for the usual colorimetric confirmation of tin, a more concentrated solution of nonlabeled $PhSn^{3+}$ was prepared in a second experiment as described in the Experimental Section above. The resulting aqueous concentrate gave a broad spot on TLC near the origin which yielded only a faint blue color upon spraying with PCV; $PhSn^{3+}$ was readily detectable at R_f 0.02. The lack of strong PCV response is typical of organotins with three or four covalent bonds (Table I) and thus provides further evidence for a (polymeric) substance in which the tin is strongly bonded. When the potassium hydroxide eluant of the resin and the remaining aqueous concentrate were analyzed by colorimetry after fusion, 15 and 9 μg, respectively, of tin was found. We therefore conclude that a polymeric tin-containing substance was indeed formed.

The formation of a polymeric substance is one explanation for the poor mass balance obtained in the photochemical studies where other explanations such as loss by volatilization, wall adsorption, and formation of chromatographable products had been experimentally excluded. While the experiments described above are consistent with a complex (polymeric) product of diphenyl and monophenyltin degradation, details of its composition and behavior remain undetermined. It appears that a complex product was formed—a product not anticipated from the previously proposed mechanism.

Based upon the laboratory experiments described here, introduction of triphenyltin hydroxide to the aqueous environment should result in degradation via photolysis to diphenyltin oxide accompanied by further degradation to water-soluble polymeric tin species.

ACKNOWLEDGMENT

We appreciate the helpful suggestions of James Swinehart, James Seiber, and Richard Fish, and the technical assistance of Peter Landrum.

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Received for review March 19, 1979. Accepted August 10, 1979. The research was supported, in part, by a grant from the California Rice Research Foundation.

Bioorganotin Chemistry. Microsomal Monooxygenase and Mammalian Metabolism of Cyclohexyltin Compounds Including the Miticide Cyhexatin

Ella C. Kimmel, John E. Casida,* and Richard H. Fish[1]

Metabolism of cyclohexyltriphenyltin by the rat liver microsomal monooxygenase system yields *trans*-2-, *cis*-3-, *trans*-3-, and *trans*-4-hydroxycyclohexyltriphenyltin and the analogous 3- and 4-keto derivatives. The major product is *trans*-4-hydroxycyclohexyltriphenyltin. Cyclohexyldiphenyltin acetate in this microsomal system gives *trans*-2-hydroxycyclohexyldiphenyltin acetate as the principal metabolite plus the 3- and 4-hydroxy compounds. Metabolites of these ^{14}C-labeled substrates were identified by TLC cochromatography with unlabeled standards from synthesis except for *trans*-2-hydroxycyclohexyldiphenyltin acetate which was degraded to cyclohexene for determination as its oxymercuration adduct. Metabolism of tricyclohexyltin hydroxide, the important miticide cyhexatin or Plictran, yields products with the anticipated chromatographic properties for 2-, 3-, and 4-hydroxycyclohexyldicyclohexyltin derivatives. The 2-hydroxy metabolite is readily degraded to cyclohexene and dicyclohexyltin compounds. Chemical ionization mass spectrometry supports the identity of the 3- and 4-hydroxycyclohexyldicyclohexyltin derivatives. Products with chromatographic properties similar to the microsomal metabolites are present in the feces of rats, mice, guinea pigs, and rabbits orally administered [^{14}C]cyhexatin.

The miticide tricyclohexyltin hydroxide (cyhexatin or Plictran) is not readily absorbed from the gastrointestinal tract of rats, dogs, sheep, and cattle and its principal or only metabolic pathway in these species is reported to be sequential destannylation, i.e., $Cy_3SnOH \rightarrow Cy_2SnO \rightarrow CySnO_2H \rightarrow Sn^{4+}$ (Blair, 1975). Destannylation mechanisms for tetra- and tributyltin derivatives in microsomal monooxygenase systems include 1- and 2-carbon hydroxylation and subsequent degradation to 1-butanol and 1-butene, respectively, and the tri- and dibutyltin derivatives (Fish et al., 1976). Microsomal oxidation also occurs at the 3 and 4 positions of tetra- and tributyltin derivatives, yielding biologically active 3-hydroxy-, 3-keto-, and 4-hydroxybutyldibutyltin derivatives (Aldridge et al., 1977). Analogous reactions involving hydroxylation at each carbon atom might be involved with cyhexatin (Casida et al., 1971; Kimmel et al., 1977).

The present study first examines microsomal monooxygenase metabolism of [^{14}C]cyclohexyltriphenyltin and [^{14}C]cyclohexyldiphenyltin acetate for two reasons: the phenyl group does not undergo significant hydroxylation (Kimmel et al., 1977) so the cyclohexyl substituent is likely to be the dominant site for metabolism; several of the possible hydroxy and keto metabolites are available as standards from synthesis (Fish and Broline, 1978) and their TLC properties and stability are known (Fish et al., 1978). It then considers microsomal and in vivo metabolism of [^{14}C]tricyclohexyltin hydroxide.

MATERIALS AND METHODS

Thin-Layer Chromatography (TLC). Silica gel 60 chromatoplates (0.25-mm gel thickness, 20 × 20 cm, Merck) were used for one- or two-dimensional development with detection of organotin derivatives and ^{14}C compounds as previously reported (Kimmel et al., 1977). Tetraorganotin derivatives were separated with four solvent

Pesticide Chemistry and Toxicology Laboratory, Department of Entomological Sciences, University of California, Berkeley, California 94720.
[1]Present address: Energy and Environment Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

0021-8561/80/1428-0117$01.00/0