were obtained by using sodium sulfate as the antifoaming agent.

The inherent volatility of the organic compounds in this study made it necessary to prepare the tissue sample for purging without volatilization of these materials. The appartus described in phase II allows the sample preparation to be carried out in a closed system; however, a more detailed evaluation of the operational variables for the apparatus described in phases I and II would be necessary prior to their use as valid analytical tools.

Registry No. Carbon disulfide, 75-15-0; methanol, 67-56-1; chloroform, 67-66-3; bromochloromethane, 74-97-5; 1,1,1-trichloroethane, 71-55-6; 1,2-dichloroethane, 107-06-2; benzene, 71-43-2; carbon tetrachloride, 56-23-5; trichloroethylene, 79-01-6; 1,2-dichloropropane, 78-87-5; dibromomethane, 74-95-3; bromodichloromethane, 75-27-4; toluene, 108-88-3; 1,1,2-trichloroethane, 79-00-5; dibromochloromethane, 124-48-1; tetrachloroethylene, 127-18-4; chlorobenzene, 108-90-7; ethylbenzene, 100-41-4; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; bromoform, 75-25-2; styrene, 100-42-5; 1,1,2,2-tetrachloroethane, 79-34-5; 1,3-dichlorobenzene, 541-73-1; 1,2-dichlorobenzene, 95-50-1; 1-chloro-3-ethoxypropane, 36865-38-0; 1-chloro-2-ethoxyethane, 628-34-2; 1,1-dichloroethane, 75-34-3.

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Degradation of the Tri-*n*-butyltin Species in Water

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Some physical and chemical characteristics of the tri-*n*-butyltin moiety from bis(tri-*n*-butyltin) oxide (TBTO) are reported that indicate that it may be moderately persistent in water. The tri-*n*-butyltin species dissolved in water neither volatilizes nor loses butyl groups over a period of at least 2 months in the dark at 20 °C; in sunlight, however, it undergoes slow ($t_{1/2} > 89$ days) photolytic decomposition, at least partially by stepwise debutylation to inorganic tin. At 20 °C, log K_{ow} of the tributyltin species is 3.2 at pH 6; for the parent TBTO at 20 °C, the aqueous solubility is 0.7–7 mg/L at pH 5–7, and the vapor pressure is estimated to be 6.4×10^{-7} mmHg.

Organotin compounds are used in three major ways, viz., as thermal stabilizers for poly(vinyl chloride), as catalysts in the production of polyurethane foams, and as biocides (Zuckerman et al., 1978). The increasing annual usage of organotin compounds raises the possibility of environmental pollution. Organotin compounds are a chemical class about which more information is sought under Canada's Environmental Contaminants Act (Canada Department of Environment and Department of National Health and Welfare, 1979) regarding toxicology and environmental fate. We chose to determine the aquatic fate of bis(tri-*n*-butyltin) oxide (TBTO) and have recently reported the occurrence of butyltin species in Ontario lakes and rivers (Maguire et al., 1982). Concurrent with our field studies in an attempt to estimate the aquatic persistence of TBTO by determining the relative importance of a variety of routes of degradation and dissipation. This article deals with (i) basic properties such as aqueous solubility, vapor pressure, and octanol–water partition coefficient and (ii) aqueous stability and volatilization from, and photolysis in, water.

The structure of TBTO in water deserves comment at this point, and a conclusion may be drawn from several indirect lines of evidence. First, it appears that TBTO dissolved in water yields the same species as do other Bu_3SnX (Bu = *n*-butyl) compounds. Support for this contention comes from (i) observations that the thin layer (Fish et al., 1976; Kimmel et al., 1977) and high-performance liquid (Jewett and Brinckman, 1981) chromatographic behavior of Bu_3SnX compounds (X = F, Cl, Br, OAc, and $OSnBu_3$) is independent of the nature of X, probably because of anion exchange on chromatography in acidic solvents, (ii) the observation of Fish et al. (1976) that the nature of the metabolites of Bu_3SnX (X = Cl, OAc, and $OSnBu_3$) produced by rat liver microsomal monooxygenase at pH 7.4 is independent of X, and (iii) observations that the variation of X within any particular series of R_3SnX compounds usually has little effect on the biological activity [e.g., Davies and Smith (1980)]. By analogy with the more soluble lower trialkyltin compounds (Tobias, 1966, 1978), therefore, the dissolution of TBTO in pure water likely produces the hydrated Bu_3Sn^+ ion, which behaves as a simple monoprotic acid [in 44% ethanol the pK_a is 6.58 (Janssen and Luijten, 1963)]. For brevity, the tri-*n*-butyltin, di-*n*-butyltin, and n-butyltin species are referred to in this article as though they existed only in cationic form (e.g., Bu_3Sn^+), since we were more interested in debutylation reactions than in cation hydrolysis, largely because in general the toxicity of butyltin compounds decreases with decreasing number of butyl groups (Davies and Smith, 1980). It is recognized that for Bu_3Sn^+ dissolved in water, phenomena such as partitioning into or-

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ganic solvents, adsorption to Teflon, and volatilization will involve not the solvated cation but, e.g., either TBTO or a halide or organic complex of Bu_3Sn^+, depending upon the nature and concentration of other solutes.

EXPERIMENTAL SECTION

Materials. TBTO (97%), tri-*n*-butyltin chloride (97%), di-*n*-butyltin dichloride (96.5%), *n*-butyltin trichloride (95%), tin (99.99%), 48% HBr, methylmagnesium bromide and *n*-pentylmagnesium bromide in diethyl ether were obtained from Ventron (Danvers, MA) (three different lots of *n*-pentylmagnesium bromide purchased after this work was completed were found to contain unacceptably high concentrations of the four butylpentyltin compounds, $Bu_nPe_{4-n}Sn$). All butyltin compounds were purified by passage in hexane through a 60 cm × 1.5 cm i.d. column of activated Florisil (Fisher Scientific Co., Toronto, Ontario, Canada), and were judged pure by gas chromatography of their pentyl derivatives (cf. below) with flame photometric, flame ionization, and electron capture detectors. Tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one) was from Aldrich (Milwaukee, WI) and was recrystallized (mp 52 °C, uncorrected) from diethyl ether before use. All organic solvents were pesticide grade from Caledon laboratories (Georgetown, Ontario Canada), and all mineral acids were Aristar grade from BDH Chemicals (Toronto, Ontario Canada). Water was distilled and passed through a "Milli-Q" system (Millipore, Ltd., Mississauga, Ontario, Canada). Fulvic acid was extracted from the water of Wylde Lake, Ontario, Canada (43° 55′ N, 80° 25′ W), an extensive boggy area at the southern end of Luther Lake that in turn discharges into the Grand River. After acidification, the water was passed through a column containing XAD-2 resin (Mantoura and Riley, 1975). The column was eluted with CH_3OH–NH_4OH (1:1 v/v) and the eluate evaporated under vacuum to dryness. All other chemicals were reagent grade and were used without further purification.

Analysis of Butyltin Species and Inorganic Tin in Water. Bu_3Sn^+, Bu_2Sn^{2+}, $BuSn^{3+}$, and inorganic tin were analyzed as *n*-pentyl derivatives, $Bu_nPe_{4-n}Sn$, by gas chromatography with a modified flame photometric detector (Maguire and Huneault, 1981). Typically, to 2 mL of an aqueous solution of butyltin species and inorganic tin 1 mL of concentrated HCl and 1 mL of 48% HBr were added, and the aqueous solution was extracted with 2 × 25 mL aliquots of 1% tropolone in benzene; the benzene extract was then derivatized and analyzed as described previously (Maguire and Huneault, 1981). This procedure yields quantitative recoveries for Bu_3Sn^+ (from either TBTO or Bu_3SnCl), Bu_2Sn^{2+}, and $BuSn^{3+}$ at pH 1–7; although Sn(IV) at pH 1 can be recovered quantitatively by this method, recoveries are low and variable at pH 5–7, probably because unextractable SnO_2 is formed. The $KHSO_4$ fusion method of Soderquist and Crosby (1978) was occasionally used to solubilize Sn(IV) from SnO_2, and this Sn(IV) in acid solution was extracted and analyzed as described above.

Although Sn(IV) was the only inorganic tin species for which recoveries were determined, the inorganic tin present in the reaction samples is reported as total recoverable inorganic tin, Sn, since it has been shown that hydride derivatization of either Sn(IV) or Sn(II) yields SnH_4 (Brinckman et al., 1981), and thus any Sn(II) that may be present in aqueous solutions may similarly be pentylated to Pe_4Sn.

In some experiments in which Bu_3Sn^+ did not undergo debutylation (e.g., in the determination of the solubility of TBTO in water), it was simply extracted with hexane, methylated with methylmagnesium bromide, and analyzed as Bu_3MeSn. The recovery is quantitative, and this modification has the advantage that the Grignard reaction need not be carried out under reflux but is simply done by stirring for 30 min at room temperature.

Vapor Pressure and Aqueous Solubility of TBTO. The vapor pressure of TBTO at 20 °C was estimated by the kinetic comparative method of Dobbs and Grant (1980), with pentachlorophenol as the reference compound. TBTO was analyzed as described above; pentachlorophenol was methylated with diazomethane and analyzed by gas chromatography with an electron capture detector.

To determine the aqueous solubility of TBTO, the inside surface of a volumetric flask was coated with 1 mL of a concentrated solution of TBTO in hexane. The hexane was evaporated under a gentle stream of nitrogen while the flask was rotated, leaving a film of TBTO, and the flask was filled with water. The contents were stirred for 4 days with a glass-coated magnetic stirring bar and then centrifuged at 2000 rpm for 1 h. A 5-mL sample was extracted with hexane and analyzed as indicated above. This experiment was done in triplicate at various pH values between 2 and 10.8, in buffers of ionic strength 0.05 M.

Adsorption of Bu_3Sn^+ to Glass and Teflon. Preliminary work had indicated adsorption of Bu_3Sn^+ from water onto Teflon-coated magnetic stirring bars.

Pyrex centrifuge tubes of 15-mL capacity were filled with aqueous Bu_3Sn^+ solutions and a Teflon strip (10 × 1 × 0.02 cm) was added to each tube. The tubes were allowed to stand for 24 h at room temperature with occasional shaking. After 24 h the Teflon strips were removed and extracted with hexane in new tubes for 48 h. The water was drained from the original tubes and the tubes were rinsed with fresh water. The combined water aliquots were extracted with hexane. Finally, the original tubes were filled with hexane and allowed to stand for 48 h to leach any Bu_3Sn^+ that had adsorbed to the glass. The hexane extracts were analyzed as described above. The adsorption experiments were done in triplicate at 0.2, 1.0, and 2.0 mg/L Bu_3Sn^+.

Octanol–Water Partition Coefficient of Bu_3Sn^+. The 1-octanol–water partition coefficient (K_{ow}) for Bu_3Sn^+ at pH 6.0 and 20 °C was measured by equilibrating the 1-octanol with water, each saturated with the other; these were then shaken with a small quantity of TBTO, centrifuged at 2000 rpm for 1 h, and sampled. Each phase was analyzed for Bu_3Sn^+ as indicated in the solubility determination above. Centrifugation was done to avoid the formation of an emulsion that might have been sampled as part of the water layer; Platford et al. (1982) have shown that centrifugation can make a difference of a factor of 30 in the value of some 1-octanol–water partition coefficients.

Volatilization of Bu_3Sn^+ from Water. Fifty-milliliter samples of an aqueous Bu_3Sn^+ solution (2 mg/L) were placed in 30 50-mL Erlenmeyer flasks that were kept in the dark at 20 °C in a cupboard that was only opened to take samples. Sampling was done in triplicate. At each sampling time the whole volume of water in each flask was extracted with hexane, and the inside of the Erlenmeyer flask was washed thoroughly with hexane to remove any Bu_3Sn^+ adhering to the glass surface. The two extracts were combined and analyzed as described above.

Aqueous Stability of Bu_3Sn^+. Aqueous stability is defined here in terms of debutylation of Bu_3Sn^+. Aqueous Bu_3Sn^+ solutions in volumetric flasks were incubated in the dark at 20 °C for various periods. At each sampling time the whole volume of water and the inside surface of

Table I. Variation of Aqueous Solubility of TBTO with pH

pH		solubility, mg/L
2.0	glycine hydrochloride	60 ± 3
2.4	glycine hydrochloride	37 ± 1
2.6	glycine hydrochloride	30 ± 2
2.8	glycine hydrochloride	22 ± 2
3.0	formate	12 ± 2
4.0	acetate	10 ± 1
5.0	acetate	7 ± 1
5.6	acetate	5 ± 2
6.0	phosphate	0.75 ± 0.5
6.6	phosphate	0.75 ± 0.5
7.0	phosphate	4 ± 1
7.6	phosphate	1 ± 0.5
7.8	phosphate	1.5 ± 0.5
8.1	Tris-HCl	31 ± 1
9.2	Tris-HCl	29 ± 2
10.0	glycinate	18 ± 6
10.8	carbonate	14 ± 1

the volumetric flask were extracted with hexane and the extracts were analyzed as indicated above. Samples were taken in triplicate and the experiment was performed at pH 2.9, 6.7, and 10.3.

Photolysis of Butyltins in Water. *Under Ultraviolet Irradiation.* Ultraviolet spectra of Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$ were obtained with a Cary 14 spectrophotometer and compared with an average spectral distribution for sunlight (Zepp and Cline, 1977). On the basis of this comparison, the following experiments were performed: (i) direct photolysis at 300 nm of $BuSn^{3+}$, Bu_2Sn^{2+}, and Bu_3Sn^+, (ii) photolysis of Bu_3Sn^+ at 300 nm sensitized with 15 mg/L fulvic acid, a photosensitizer found in some natural waters, and (iii) direct and fulvic acid sensitized photolyses of Bu_3Sn^+ at 350 nm. Solutions of the tin species in water or 10% (v/v) acetonitrile [a solvent that is not a photosensitizer (Smith et al., 1977)] were irradiated in a water-cooled cylindrical quartz cell, 2-cm i.d., by using a Rayonet photochemical reactor (Southern New England Ultraviolet Co., Hamden, CT). The photoreactor was equipped with fluorescent-coated mercury lamps with peak intensities at 300 nm (RPR-3000 A) or 350 nm (F8T5BLB) and half-bandwidths of 30 nm. Solutions were not deaerated. Samples of the photolysis solutions were acidified, extracted with 1% tropolone in benzene, and analyzed as indicated above. Appropriate dark controls were used in all cases. Light intensities were determined by the ferrioxalate actinometric method of Hatchard and Parker (1956).

In Sunlight. Pyrex centrifuge tubes containing solutions of Bu_3Sn^+ in Hamilton Harbour water or distilled water were exposed to sunlight on the roof of the laboratory for periods of up to 3 months in the summer of 1981. The tubes had ground-glass stoppers and were sealed with Teflon tape. Periodically the whole volume of water in a tube, along with the inside surface of the tube, was extracted with tropolone in benzene and analyzed as indicated above. The water that had been extracted was replaced in its original tube and evaporated to dryness, and the residue fused with $KHSO_4$ (Soderquist and Crosby, 1978). The residue was dissolved in acid and extracted and analyzed as indicated above. Appropriate dark controls were used.

RESULTS AND DISCUSSION

Vapor Pressure and Aqueous Solubility of TBTO. The rate of loss curves for both TBTO and pentachlorophenol were exponential within experimental error, and when a value of 5×10^{-6} mmHg was used for the vapor pressure of pentachlorophenol (Dobbs and Grant, 1980),

Table II. Recovery of Bu_3Sn^+ from Water, Teflon, and Glass at Three Concentrations

$[Bu_3Sn^+]_{initial}$, mg/L	% recovery			
	water	Teflon	glass	total
2.22	79 ± 5	6 ± 1	6 ± 2	91
1.10	67 ± 16	18 ± 5	6 ± 2	91
0.24	53 ± 5	21 ± 3	67 ± 17	141

Table III. Recovery of Bu_3Sn^+ in Volatilization Experiment

time, day(s)	$[Bu_3Sn^+]$,[a] mg/L
0	1.0 ± 0.2
1	1.0 ± 0.1
2	1.1 ± 0.1
4	0.8 ± 0.4
8	0.9 ± 0.1
16	1.0 ± 0.3
30	1.1 ± 0.1
62	1.0 ± 0.1

[a] Corrected to original solution volume of 50 mL; 20% of the water evaporated over 62 days.

a value of $(6.4 \pm 1.2) \times 10^{-7}$ mmHg was estimated for the vapor pressure of TBTO at 20 °C.

Table I shows that the aqueous solubility of TBTO is at a minimum of 0.75 mg/L at pH 6.0–6.6 and increases with both decreasing and increasing pH. We assume that these results are largely unaffected by adsorption of Bu_3Sn^+ from water to glass (cf. below) since concentrated TBTO solutions in hexane were initially used to coat the insides of the flasks, and the solubilities are greater than 1 mg/L in most cases anyway.

Adsorption of Bu_3Sn^+ to Glass and Teflon. Table II summarizes the adsorption results. At 2.2 mg/L most of the Bu_3Sn^+ is dissolved in water, but below this concentration relatively more Bu_3Sn^+ is adsorbed to the Teflon and the glass, and the variability of recovery values becomes larger. These results may vary from vessel to vessel, but the general conclusion is that glass and Teflon can adsorb trace quantities of Bu_3Sn^+ from pure water and that care must be taken to rinse with organic solvents all glass and Teflon surfaces with which Bu_3Sn^+ has come into contact to ensure maximum recovery.

Octanol–Water Partition Coefficient of Bu_3Sn^+. log K_{ow} was determined to be 3.19 ± 0.05 at pH 6.0, but this value may be affected by adsorption to glass since the aqueous solubility to TBTO at pH 6 is less than 1 mg/L; a log K_{ow} value of 3.2 suggests a moderate potential for bioaccumulation.

Volatilization of Bu_3Sn^+ from Water. The constant recoveries of Bu_3Sn^+ shown in Table III demonstrate that there was no volatilization of Bu_3Sn^+ from water over a period of 62 days, even though 20% of the water had evaporated. It might be argued that Bu_3Sn^+ did not volatilize from water since it was adsorbed to the glass, but the results of Table II show that at 1 mg/L most of the Bu_3Sn^+ is dissolved in the water; in any event, in natural waters the presence of dissolved and particulate matter will probably serve to slow the volatilization even more.

Aqueous Stability of Bu_3Sn^+. The constant recoveries of Bu_3Sn^+ over the course of the experiment, shown in Table IV, show that there is no cleavage of butyl groups from tin over 63 days at 20 °C in the dark at pH values between 2.9 and 10.3.

Sheldon (1975) postulated that bis(tri-*n*-butyltin) carbonate could be produced in water by the reaction of Bu_3Sn^+ with dissolved CO_2. If such a reaction occurred during the course of 63 days, its occurrence might have been obscured if the Bu_3Sn^+ moiety were as readily ex-

Table IV. Stability of Bu_3Sn^+ in Aqueous Solution at Various pH Values[a]

time, day(s)	$[Bu_3Sn^+]$, mg/L		
	pH 2.9	pH 6.7	pH 10.3
0	2.1 ± 0.3	1.3 ± 0.4	5.8 ± 0.9
1	2.4 ± 0.2	1.1 ± 0.1	6.3 ± 0.2
2	2.1 ± 0.4	1.0 ± 0.2	5.9 ± 0.4
4	1.9 ± 0.3	1.4 ± 0.5	5.9 ± 0.3
8	2.3 ± 0.1	1.2 ± 0.2	5.8 ± 0.2
15	2.2 ± 0.4	1.0 ± 0.1	5.9 ± 0.8
31	2.1 ± 0.2	1.2 ± 0.3	6.0 ± 0.1
63	2.2 ± 0.3	1.4 ± 0.2	5.9 ± 0.4

[a] Solution stored in the dark at 20 °C.

Table V. Extinction Coefficients of Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$ in the Ultraviolet Region[a]

λ, nm	ε, L mol⁻¹ cm⁻¹		
	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$
360	0.06	0.03	0.07
350	0.10	0.04	0.08
340	0.16	0.05	0.10
330	0.26	0.06	0.23
320	0.40	0.07	0.54
310	0.64	0.10	1.21
300	0.98	0.16	2.38
290	1.62	0.29	3.53
280	2.72	0.75	3.73

[a] Spectra were obtained in 10% (v/v) methanol vs. 10% (v/v) methanol at 20 °C

tractable as it is from other Bu_3SnX compounds.

Photolysis of Butyltins in Water. Table V shows the extinction coefficients of Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$. The butyltins weakly absorb the small component of sunlight in the 300-nm region ($0.1 < \epsilon < 5$), very weakly absorb light in the 350-nm region ($0.01 < \epsilon \leq 0.1$) and essentially transmit the remainer of the sunlight spectrum ($\epsilon < 0.01$). Thus, only the near-UV component of sunlight could cause the direct photodegradation of butyltins in surface waters. The relative photoreactivities of these compounds were determined at 300 and 350 nm in the photoreactor. Table VI summarizes the kinetic results of all photolyses.

At 300 and 350 nm. Figure 1 shows that, within experimental error, the concentration of $BuSn^{3+}$, which was exposed to 300-nm light, declined exponentially ($BuSn^{3+}$ in the dark at 20 °C is stable for at least 10 days). At the end of the experiment, the concentration of inorganic tin accounted for about 70% of the initial $BuSn^{3+}$ concentration.

Figure 2 shows that the photolytic decomposition of Bu_2Sn^{2+} proceeds much more slowly than that of $BuSn^{3+}$. There was about 30% decomposition in 9 days, at which time the sum of the concentrations of the products, $BuSn^{3+}$ and inorganic tin, was roughly equal to that lost by Bu_2Sn^{2+}. Although there was significant variability in the concentrations of the dark control with time, it appeared that there was no decomposition of Bu_2Sn^{2+} in the dark at 20 °C over 9 days.

Figure 3 shows an exponential decline with time in concentration of Bu_3Sn^+ at 300 nm. After 9 days the sum of the concentrations of the only identified products,

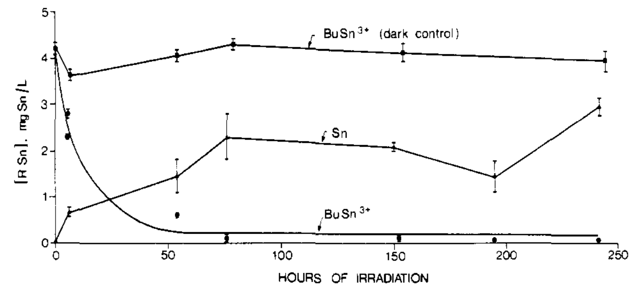

Figure 1. Photolysis of $BuSn^{3+}$ in 90% water–10% (v/v) acetonitrile at 300 nm. The exponential curve was calculated by a nonlinear least-squares computer program.

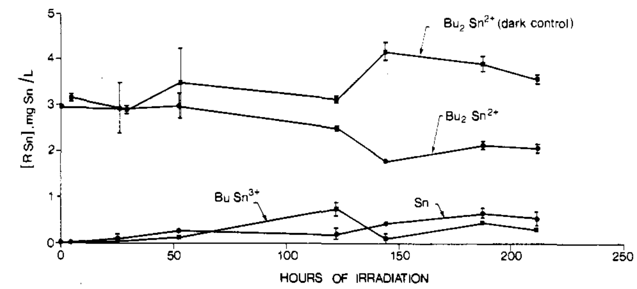

Figure 2. Photolysis of Bu_2Sn^{2+} in 90% water–10% (v/v) acetonitrile at 300 nm.

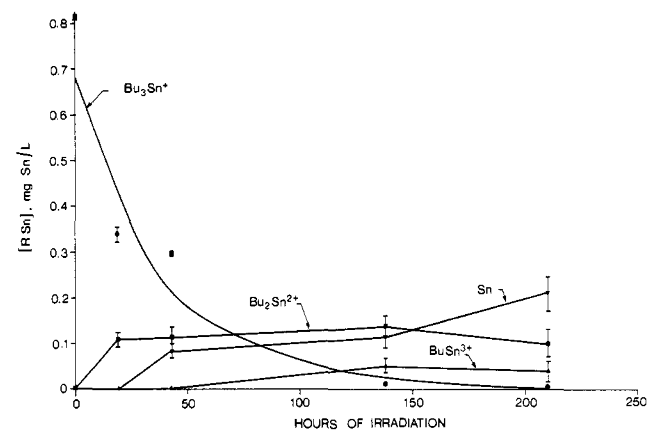

Figure 3. Photolysis of Bu_3Sn^+ in water at 300 nm. The exponential curve was calculated by a nonlinear least-squares computer program.

Table VI. Half-Lives for Photolysis of Butyltins

species	conditions	$t_{1/2}$, day(s)	product recovery, % of starting material, at end of experiment
$BuSn^{3+}$	300 nm	0.4 ± 0.1	68
Bu_2Sn^{2+}	300 nm	>9	84
Bu_3Sn^+	300 nm	1.1 ± 0.2	40
Bu_3Sn^+	300 nm, sensitized (15 mg/L fulvic acid)	0.6 ± 0.2	65
Bu_3Sn^+	350 nm	>18	60
Bu_3Sn^+	350 nm, sensitized (15 mg/L fulvic acid)	6.2 ± 1.8	58
Bu_3Sn^+	sunlight, in Hamilton Harbour water or distilled water	>89 (>4 × 10^4 langleys)	76

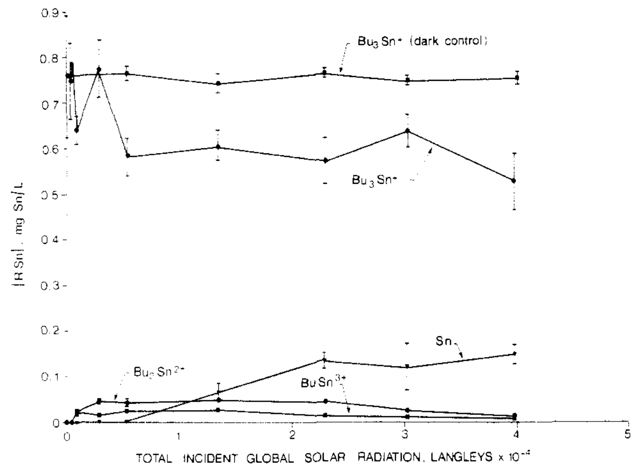

Figure 4. Sunlight photolysis of Bu_3Sn^+ dissolved in Hamilton Harbour water.

Bu_2Sn^{2+}, $BuSn^{3+}$ and inorganic tin, equalled about 40% of that lost by Bu_3Sn^+. As seen above, Bu_3Sn^+ does not lose butyl groups in the dark for at least 2 months.

The degradation of Bu_3Sn^+ at 300 and 350 nm was measurably enhanced by the presence of 15 mg/L fulvic acid. Under the experimental conditions, the fulvic acid adsorbed about 30% of the incident radiation at 300 nm and about 15% at 350 nm. Thus, if fulvic acid were not capable of stimulating the photolysis of Bu_3Sn^+, the disappearance half-life should have increased because less light was reaching the tin compound. Instead, the disappearance half-life was reduced to 0.6 from 1.1 days at 300 nm and to 6.2 from 18 days at 350 nm.

In Sunlight. Figure 4 shows that the photolysis of Bu_3Sn^+ in sunlight is a fairly slow process, with a "half-life" of $>4 \times 10^4$ langleys, corresponding to >89 days in the summer of 1981. Within experimental error the results in distilled water were the same as those in Hamilton Harbour water. The sum of the concentrations of the identified products, Bu_2Sn^{2+}, $BuSn^{3+}$, and inorganic tin, accounted for 75% of the loss in Bu_3Sn^+ concentration at the end of the experiment. This improved recovery was due to differences in experimental design (i.e., the use of individual test tubes rather than a single photoreactor from which samples were periodically withdrawn) that allowed (i) the whole volume of water in each test tube to be extracted, along with the inside surface of the tube, with tropolone in benzene and (ii) the extracted water to be replaced in the original tube and evaporated to dryness and the residue to be fused with $KHSO_4$. The contribution to the recovery of inorganic tin from the $KHSO_4$ fusion step amounted to 25–50% of the total inorganic tin, but the fusion technique does not differentiate SnO_2 from any water-soluble polymeric butyltin that may result from photolysis (cf. below).

In the apparatus used for our irradiations, accurate quantum yields of such weakly absorbing compounds as Bu_3Sn^+ are very difficult to obtain. However, by estimating an average path length of 1.2 cm and determining light intensities by ferrioxalate actinometry (Hatchard and Parker, 1956) we obtained a value of 0.3 for the disappearance quantum yield of Bu_3Sn^+, which is probably within 30% of the true value.

On the basis of these results, the route of direct photolysis of Bu_3Sn^+ in water appears to involve sequential debutylation to inorganic tin. The mechanism may be analogous to the free radical mechanism proposed by Soderquist and Crosby (1980) for the photolysis of triphenyltin hydroxide in water. The poor mass balance at the end of some of our photoreactor experiments may be due to (i) a competing process such as formation of water-soluble butyltin polymers such as those proposed by Soderquist and Crosby (1980) in the photolysis of triphenyltin hydroxide and/or to (ii) precipitation of SnO_2 and adsorption of butyltins to the surface of the photoreactor at concentrations less than 1 mg/L.

If it proves to occur in natural waters, the promotion of the photolysis by fulvic acid may effectively increase the range of wavelengths active in the photodegradation of Bu_3Sn^+. However, in view of the similarity between the sunlight photolysis experiments in distilled water and Hamilton Harbour water, which contains little fulvic acid, these results should be extended cautiously. It is of interest to note that although Soderquist and Crosby (1980) observed that the photolysis of triphenyltin hydroxide could be sensitized by either acetone or rose bengal, no enhancement was seen in rice-field water, a medium in which several compounds stable in distilled water in sunlight had been observed to undergo accelerated photodegradation (Soderquist et al., 1977; Ross and Crosby, 1973).

In summary, although the sunlight photolysis of Bu_3Sn^+ in natural water is fairly slow ($t_{1/2} > 89$ days), the absence of other faster degradation processes may make photolysis the significant route of Bu_3Sn^+ degradation in water. Further work on Bu_3Sn^+ adsorption to sediments, bacterial degradation, and uptake by fish and algae is in progress.

Registry No. Bis(tri-*n*-butyltin) oxide, 56-35-9; tri-*n*-butyltin chloride, 1461-22-9; di-*n*-butyltin dichloride, 683-18-1; *n*-butyltin trichloride, 1118-46-3; Teflon, 9002-84-0; Bu_3Sn^+, 36643-28-4.

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Photolysis Rates of (2,4,5-Trichlorophenoxy)acetic Acid and 4-Amino-3,5,6-trichloropicolinic Acid in Natural Waters

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Photoreactions of (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) and 4-amino-3,5,6-trichloropicolinic acid (picloram) were studied in distilled water, natural water samples, fulvic acid solutions, and solutions containing iron (III) and/or hydrogen peroxide to determine the effects of dissolved natural substances on the photolysis rates of these herbicides. Most of the experiments were conducted with sunlight as the light source and with dilute solutions of 3,4-dichloroaniline (DCA) as an outdoor actinometer. When reaction quantum yields determined in this study were used, near-surface half-lives for direct photolysis were computed to be 15 days for 2,4,5-T and 2.2 days for picloram during late summer at latitude 40° N, in close agreement with observed values. Humic substances in natural water samples and a commercial fulvic acid enhanced near-surface photolysis rate constants of 2,4,5-T with similar efficiencies, as indicated by the linear dependence of the rate constants on the UV absorbance of the waters. 2,4,5-Trichlorophenol was a major product of the humic-induced photoreactions. Humic substances, even at the highest concentrations usually observed in natural waters, had only a minor enhancing effect on the photolysis rate of picloram. Preliminary studies indicated that photocatalytic processes involving iron species and peroxides may contribute to the sunlight-induced reaction of 2,4,5-T in acidic, weakly absorbing natural waters.

A number of recent studies have examined the influence of natural substances on photochemical transformations in aquatic systems (Draper and Crosby, 1981; Mill et al., 1980; Zepp et al., 1981). Such studies, with varying degrees of success, have considered effects of natural substances on the photoproducts and defined relationships between water composition and photolysis rate. The present work was performed as part of an environmental exchange agreement between the United States and the Soviet Union in an attempt to develop better kinetic equations and to further examine their generality. (2,4,5-Trichlorophenoxy)acetic acid (2,4,5-T) and 4-amino-3,5,6-trichloropicolinic acid (picloram) were chosen for study based on considerations of their direct light absorption rates, analytical methodologies, and previous photochemical data.

Both 2,4,5-T and picloram are herbicides that are used to control undesirable brush and woody plants. Although it has been suggested that sunlight-induced photoreactions of 2,4,5-T (Kenaga, 1974; Crosby and Wong, 1973) and picloram (Hedlund and Youngson, 1972) make a significant contribution to the environmental dissipation of these herbicides, few studies have focused on their photochemical behavior in natural waters.

Previous research has indicated that the photochemistry of 2,4,5-T and picloram may occur by several pathways. The direct absorption of sunlight by these chemicals leads to loss of ring chlorines as well as other reactions (Crosby and Wong, 1973; Glass, 1975; Hall et al., 1968; Mosier and Guenzi, 1973). Various photosensitizers have been shown to accelerate the photolysis of 2,4,5-T (Crosby and Wong, 1973) and picloram (Glass, 1975), raising the possibility that natural substances in aquatic environments may sensitize the sunlight-induced degradation of these pesticides (Miller et al., 1980). Finally, studies by Mill et al. (1980) have shown that free radicals are generated upon exposure of natural waters to sunlight, and the side chains of substituted phenoxyacetic acids similar to 2,4,5-T are known to be oxidized by attack of free radicals (Brown et al., 1964).

Several studies have appeared concerning the sunlight photolysis rates of 2,4,5-T and picloram in water. Crosby and Wong (1973) reported that 17% of 2,4,5-T photodecomposed upon exposure to sunlight for 4 days, indicating a direct photolysis half-life on the order of 15 days in California summer sunlight. The thorough studies of picloram photolysis by Hedlund and Youngson (1972) indicate that this herbicide undergoes direct photolysis in sunlight about 1 order of magnitude more rapidly than 2,4,5-T. Conflicting studies have appeared concerning the quantum yields for direct photoreaction of picloram, with Mosier and Guenzi (1973) reporting a value of 0.005 at 366 nm and Glass (1975) reporting a quantum yield of 0.04 at 254 and 313 nm. No reports have appeared concerning the reaction quantum yield for 2,4,5-T in water, nor have there been any systematic studies of the photolysis rates of 2,4,5-T or picloram in natural waters.

In this report, we compare kinetic results concerning the photolysis of 2,4,5-T and picloram in distilled water and particle-free natural water samples obtained from several rivers in the United States. Results of these comparisons indicate that 2,4,5-T is considerably more susceptible to photosensitized reaction in natural water than is picloram. Evidence is presented that the humic substances in the

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