

THE ULTRAVIOLET DEGRADATION OF THE METHYLTIN CHLORIDES IN CARBON TETRACHLORIDE AND WATER

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Summary

The ultraviolet degradation of the methyltin chlorides in carbon tetrachloride and water has been quantitatively studied by ^1H NMR spectroscopy. In the organic solvent trimethyltin chloride degraded to an inorganic tin species, via di- and mono-methyltin intermediates; in water, a monomethyltin derivative was not observed. The ultraviolet breakdown of dimethyltin dichloride and monomethyltin trichloride in these solvents was also studied, and the approximate relative rates of degradation were established.

Introduction

Organotin compounds, $R_n\text{SnX}_{4-n}$, have a wide variety of industrial applications [1] and can therefore enter the environment through a number of different routes. Consequently, a knowledge of the eventual fate of these compounds is of considerable importance.

The organotin derivatives possessing the highest biological activity are the triorganotin species, $R_3\text{SnX}$, and progressive removal of the R groups, is associated with a lowering in activity, until an essentially non-toxic inorganic tin compound remains. The possibility of this process occurring in the environment is of benefit to potential organotin users, since the application of these compounds would be unlikely to lead to serious long term pollution. In addition, further impetus for studying the degradation of organotin derivatives, particularly the methyltin species, has arisen from the suggestion of the possible environmental methylation of inorganic tin [2]. One of the ways in which degradation of organotin might be accelerated is by ultraviolet (UV) irradiation, and a review of this, and other breakdown mechanisms, has recently been published [3]. However, the apparent lack of quantitative data on degradation pathways has prompted this study, by ^1H NMR spectroscopy (although not under environmental conditions) of the results of UV irradiation of the methyltin chlorides, $\text{Me}_n\text{SnCl}_{4-n}$ ($n = 1-3$), in carbon tetrachloride and in water.

Experimental

UV irradiation

UV radiation was provided by a Hanovia UVS 500 system, utilising a medium pressure mercury arc tube, which was mounted in a vertical position, so as to give an even distribution of irradiation intensity in the horizontal plane. The aqueous solutions were irradiated using an arc tube emitting wavelengths above 180 nm, although wavelengths below 200 nm were assumed to be absorbed by air. However, carbon tetrachloride absorbs UV light of wavelengths below approximately 230 nm and it is known [4] that this may lead to homolytic C–Cl bond fission:



Thus, to minimise this reaction, carbon tetrachloride solutions were irradiated using an arc tube emitting wavelengths above 235 nm.

The solutions to be irradiated were contained in stoppered silica cells (Spectrosil grade; UV cut-off 170 nm), which were positioned in an arc 22 cm from the tube. The temperature at the sample position was approximately 35°C.

The UV irradiation intensity at the cell position was measured using Ultra Violet Products, Inc., “Blak-ray” UV intensity meters which give total intensity readings over the wavelength ranges 200–300 nm and 300–400 nm.

Spectroscopic techniques

¹H NMR spectra were recorded in 5 mm tubes on a Perkin–Elmer R10 instrument at 60 MHz. Quantitative measurements of concentration were made by both integration of the NMR signal and comparison of peak heights with those obtained using standard solutions. The minimum concentration of monomethyltin trichloride which could be quantitatively determined in solution in this way was 0.005 *M*. Thus, to ensure that concentrations were mainly above the instrumental limit of detection, all irradiations were carried out on solutions having an initial organotin concentration of 0.05 *M*.

The ¹¹⁹Sn Mössbauer spectrum was obtained using a constant acceleration microprocessor spectrometer (Cryophysics Ltd.) with a 512-channel data store. A Ba^{119m}SnO₃ source was used, at room temperature, and the sample was packed in Perspex discs and cooled at 80 K using a liquid nitrogen cryostat.

UV absorption spectra were recorded on a Bausch and Lomb Spectronic 505 double beam instrument.

Tin analysis

Irradiated solutions were analysed for their total tin content by iodometric titration, after wet-ashing with nitric/sulphuric acids [5].

Results and discussion

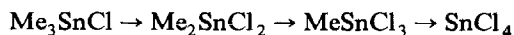
Irradiations in carbon tetrachloride

In carbon tetrachloride, the methyltin chlorides Me_{*n*}SnCl_{4-*n*} (*n* = 1–3) exist as discrete tetrahedral monomers. The ¹H NMR chemical shifts and coupling constants of these compounds in carbon tetrachloride are well established [6] and their UV

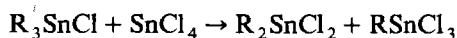
absorption spectra showed, in all cases, an absorption maximum at approximately 260 nm.

UV irradiation for appropriate periods of 0.05 *M* solutions of Me_3SnCl in carbon tetrachloride and subsequent analysis by ^1H NMR spectroscopy showed that both Me_2SnCl_2 and MeSnCl_3 were degradation products (Table 1).

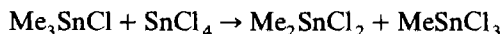
In addition, the presence of an inorganic tin species, presumably SnCl_4 , was qualitatively demonstrated by paper chromatography [7]. Since volumetric analysis revealed that the total tin content did not decrease during irradiation, the concentration of inorganic tin species produced after a given irradiation time may be calculated as being the difference between the total tin concentration and the organotin concentration, as determined by ^1H NMR spectroscopy. Figure 1 shows a plot of the UV degradation of Me_3SnCl (0.05 *M* in carbon tetrachloride (Irradiation intensity: 235–300 nm = 5 mwatts cm^{-2} ; 300–400 nm = 7 mwatts cm^{-2}), and it may be seen that a stepwise reaction occurs:



During the breakdown process, varying amounts of the methyltin chlorides and stannic chloride are present in solution simultaneously, and, since it is known [8] that the following redistribution reactions can occur:



equimolar mixtures of these methyltin compounds were prepared in carbon tetrachloride and stored at 40°C. ^1H NMR spectra of these solutions were recorded periodically for up to 14 days and the only reaction observed was that between trimethyltin chloride and stannic chloride:



However, this reaction was found to be quite slow, since after 14 days approximately 40% of the initial trimethyltin chloride still remained. Thus redistribution reactions had little or no effect on the degradation process.

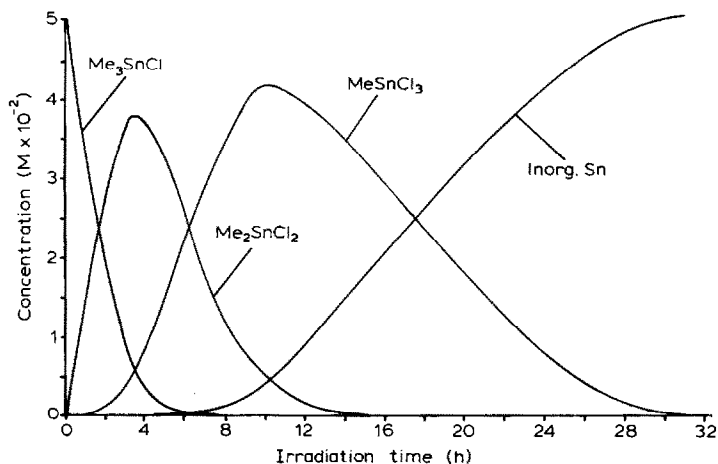


Fig. 1. The UV degradation of 0.05 *M* trimethyltin chloride in carbon tetrachloride.

TABLE I
ANALYTICAL RESULTS, BY ^1H NMR, OF THE UV DEGRADATION OF Me_3SnCl (0.05 M IN CARBON TETRACHLORIDE)

| Irradiation time (h) | N^a | Me_3SnCl | | Me_2SnCl_2 | | MeSnCl_3 | |
|----------------------|-------|--|---|--|---|--|---|
| | | Concentration b ($M \times 10^{-2}$) | Standard deviation c ($\times 10^{-2}$) | Concentration b ($M \times 10^{-2}$) | Standard deviation c ($\times 10^{-2}$) | Concentration b ($M \times 10^{-2}$) | Standard deviation c ($\times 10^{-2}$) |
| 0.0 | | 5.0 | — | — | — | — | — |
| 0.5 | 4 | 4.1 | 0.2 | 0.8 | 0.1 | — | — |
| 1.0 | 4 | 3.4 | 0.2 | 1.4 | 0.1 | — | — |
| 2.0 | 4 | 1.9 | 0.2 | 2.9 | 0.2 | — | — |
| 2.5 | 4 | 1.6 | 0.1 | 3.5 | 0.3 | — | — |
| 3.0 | 3 | 0.8 | 0.1 | 3.8 | 0.2 | 0.4 | 0.1 |
| 3.5 | 6 | 0.5 | 0.2 | 4.1 | 0.4 | 0.5 | 0.2 |
| 4.0 | 8 | 0.3 | 0.1 | 3.8 | 0.4 | 1.2 | 0.4 |
| 5.0 | 12 | — | — | 3.2 | 0.3 | 1.8 | 0.3 |
| 6.0 | 6 | — | — | 2.5 | 0.1 | 2.7 | 0.2 |
| 7.0 | 8 | — | — | 1.9 | 0.6 | 2.9 | 0.5 |
| 8.0 | 8 | — | — | 1.3 | 0.5 | 3.5 | 0.4 |
| 9.0 | 8 | — | — | 0.8 | 0.6 | 4.1 | 0.4 |
| 10 | 7 | — | — | 0.5 | — | 4.2 | 0.4 |
| 11.0 | 8 | — | — | — | — | 4.2 | 0.3 |
| 12.0 | 9 | — | — | — | — | 3.8 | 0.4 |
| 13.0 | 8 | — | — | — | — | 3.7 | 0.4 |
| 15.0 | 8 | — | — | — | — | 3.2 | 0.4 |
| 17.0 | 7 | — | — | — | — | 2.7 | 0.3 |
| 20.0 | 6 | — | — | — | — | 1.9 | 0.2 |
| 25.0 | 6 | — | — | — | — | 0.7 | 0.2 |

a Number of samples irradiated. b The figure reported is the mean value obtained for N irradiated samples. c The standard deviation of the concentration is calculated for $N - 1$ samples.

A comparison of the relative rates of breakdown of the tri-, di- and mono-methyltin chlorides in carbon tetrachloride was obtained by irradiating 0.05 *M* solutions of Me_2SnCl_2 and MeSnCl_3 , under identical conditions (UV intensity and temperature) to that of Me_3SnCl , and analysing the solutions as usual by ^1H NMR spectroscopy (Tables 2 and 3).

Figure 2 shows the breakdown of the three methyltin chlorides in carbon tetrachloride, and from the time taken for 50% of each alkyltin compound to degrade it may be estimated that the Me_3SnCl breaks down approximately twice as rapidly as Me_2SnCl_2 , which in turn reacts approximately twice as rapidly as MeSnCl_3 .

When the solutions were irradiated in silica cells and a sample then taken for NMR analysis, no species other than the organotin compounds were detected. However, the ^1H NMR spectrum of a 0.05 *M* solution of Me_3SnCl in carbon tetrachloride, irradiated in a sealed silica NMR tube which was filled virtually to the top, leaving as little free space as possible, revealed that the major non-tin containing product of the reaction was methane ($\delta(^1\text{H})$ 0.23 ppm, Lit. 0.23 ppm [9]). In fact, the formation of methane accounted for approximately 50–60% of the methyl groups cleaved from the tin atoms. The formation of alkanes from the UV irradiation of tetraorganotins in carbon tetrachloride has been observed by Razuvaev et al. [4], although the alkane was, in general, only produced when the organotin compound and the solvent were present in approximate equimolar ratios; when the solvent was in a considerable excess, the alkyl chloride was produced [4]. In the present study, however, methane was formed even in the presence of a large excess (~ 200 molar) of the solvent. Methyl chloride ($\delta(^1\text{H})$ 3.01 ppm, Lit. 3.06 ppm [9]) and ethane ($\delta(^1\text{H})$ 0.8 ppm, Lit. 0.86 ppm [9]) were detected in the solutions irradiated in sealed tubes, but in markedly smaller amounts (each accounting for about 15% of the methyl groups cleaved).

TABLE 2

ANALYTICAL RESULTS, BY ^1H NMR, OF THE UV DEGRADATION OF Me_2SnCl_2 (0.05 *M* IN CARBON TETRACHLORIDE)

| Irradiation time (h) | <i>N</i> ^a | Me_2SnCl_2 | | MeSnCl_3 | |
|----------------------|-----------------------|--|---|--|---|
| | | Concentration ^b (<i>M</i> × 10 ⁻²) | Standard deviation ^c (× 10 ⁻²) | Concentration ^b (<i>M</i> × 10 ⁻²) | Standard deviation ^c (× 10 ⁻²) |
| 0.0 | | 5.0 | — | — | — |
| 1.0 | 6 | 4.1 | 0.2 | 0.8 | 0.2 |
| 2.0 | 6 | 3.2 | 0.2 | 1.8 | 0.1 |
| 3.0 | 4 | 2.4 | 0.1 | 2.5 | 0.2 |
| 4.0 | 4 | 1.8 | 0.1 | 3.1 | 0.1 |
| 5.0 | 4 | 1.5 | 0.1 | 3.4 | 0.2 |
| 6.0 | 4 | 0.9 | 0.2 | 3.9 | 0.1 |
| 7.0 | 4 | 0.6 | 0.2 | 4.0 | 0.2 |
| 8.0 | 4 | 0.4 | 0.2 | 4.3 | 0.1 |

^a Number of samples irradiated. ^b The figure reported is the mean value obtained from *N* irradiated samples. ^c The standard deviation of the concentration is calculated for *N* - 1 samples.

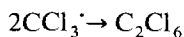
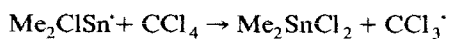
TABLE 3

ANALYTICAL RESULTS, BY ^1H NMR, OF THE UV DEGRADATION OF MeSnCl_3 (0.05 M IN CARBON TETRACHLORIDE)

| Irradiation time (h) | N^a | MeSnCl_3 | |
|----------------------|-------|--|---|
| | | Concentration b ($M \times 10^{-2}$) | Standard deviation c ($\times 10^{-2}$) |
| 0.0 | 4 | 5.0 | — |
| 2.0 | 4 | 4.3 | 0.1 |
| 4.0 | 4 | 3.6 | 0.1 |
| 6.0 | 4 | 2.7 | 0.2 |
| 8.0 | 4 | 2.4 | 0.2 |
| 10.0 | 4 | 1.6 | 0.2 |
| 12.0 | 4 | 0.9 | 0.3 |
| 14.0 | 4 | 0.6 | 0.1 |

a Number of samples irradiated. b The figure reported is the mean value obtained from N irradiated samples. c The standard deviation of the concentration is calculated for $N - 1$ samples.

From these observations, the following reaction mechanism for the degradation process may be proposed:



Since methane is the predominant non-tin containing product, hydrogen abstraction

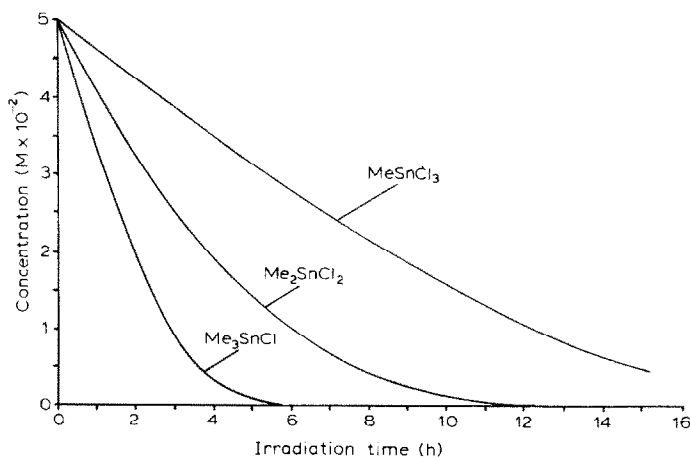
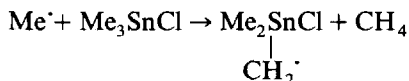
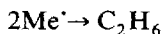
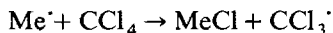


Fig. 2. The UV degradation of the methyltin chlorides, $\text{Me}_n\text{SnCl}_{4-n}$ ($n = 1-3$), in carbon tetrachloride (0.05 M solutions).

by a methyl group from an organotin molecule must occur e.g.:

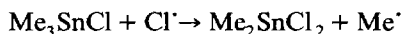


and the only other non-tin containing products presumably arise from:



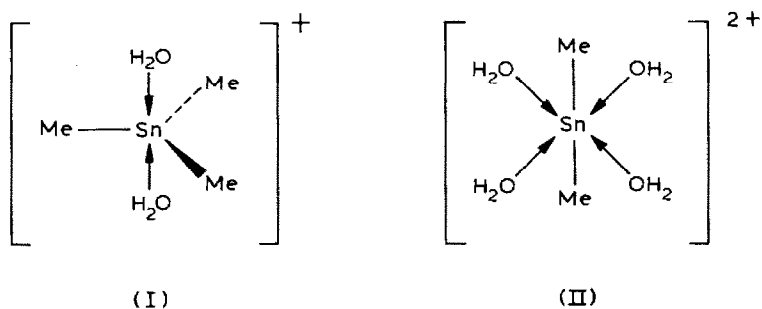
No features were seen in any of the NMR spectra to account for the products formed from the organotin radical produced after abstraction of a hydrogen atom. This species may react with the solvent or possibly dimerise, but in either case the compound produced must itself undergo fairly rapid breakdown, and thus escape detection.

It must additionally be considered that although irradiations were carried out using light of wavelengths greater than 235 nm to minimise homolytic C-Cl bond cleavage of the solvent, this reaction might still have been occurring, leading to the possibility that a percentage of the organotin chlorides were degrading because of direct substitution of the methyl groups by chlorine radicals from the solvent:

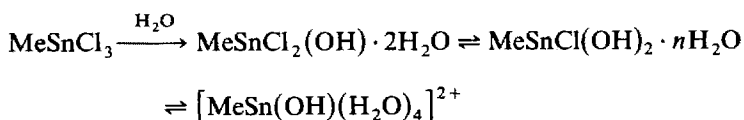


Irradiations in water

The species formed upon dissolution of the methyltin chlorides in water are dependent upon the pH and solution concentration. The pH values of 0.05 M solutions of Me_3SnCl , Me_2SnCl_2 and MeSnCl_3 in distilled water were found to be 3.6, 2.4 and 1.4, respectively, and it has been suggested that Me_3SnCl will exist in solution as the trimethyltin cation, Me_3Sn^+ , whilst Me_2SnCl_2 will be present as a mixture of the cationic dimethyltin species, $\text{Me}_2\text{Sn}^{2+}$ and $\text{Me}_2\text{Sn}(\text{OH})^+$ [10]. The tri- and di-methyltin cations have been shown [10-12] to be hydrated species and to have structures I and II, respectively. For MeSnCl_3 , however, a concentration



dependent equilibrium has been found [13,14] to exist:



The species to the right of the equilibrium are favoured at low concentrations, and a

0.05 *M* solution contains approximately 45% $\text{MeSnCl}_2(\text{OH}) \cdot 2\text{H}_2\text{O}$, 30% $\text{MeSnCl}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ and 25% $[\text{MeSn}(\text{OH})(\text{H}_2\text{O})_4]^{2+}$.

UV absorption spectra were recorded for aqueous solutions of the methyltin chlorides and it was found that Me_3SnCl showed a single peak, with an absorption maximum at 208 nm, Me_2SnCl_2 displayed two absorption maxima, at 203 and 228 nm, and MeSnCl_3 gave a single broad band, with a maximum at 220 nm. Since the absorption maxima of these compounds were in the range 203–228 nm, irradiation with light of wavelength greater than 235 nm, as with the carbon tetrachloride solutions, would result in a much slower rate of breakdown. Water does not absorb light of wavelengths < 200 nm, and so it is possible to irradiate samples with light of these wavelengths without UV induced homolysis of the solvent affecting the rate of breakdown of the organotin compound. Thus, 0.05 *M* aqueous solutions of Me_3SnCl were irradiated for appropriate periods with UV light of wavelengths upwards of 200 nm. (Irradiation intensity: 200–300 nm = 2 mwatts cm^{-2} ; 300–400 nm = 8 mwatts cm^{-2}). During irradiation, the formation of a fine white precipitate was observed, and since this would have acted as a light filter and reduced the rate of degradation, it was necessary to centrifuge the solutions from time to time.

^1H NMR chemical shifts and coupling constants, $J(^{119}\text{Sn}-^1\text{H})$, for the methyltin chlorides in aqueous solution have been reported previously [14], and spectra of the irradiated solutions of Me_3SnCl showed, in addition to the peak due to the trimethyltin cation, a resonance which was ascribed to a dimethyltin species. From the work of Tobias [10], this was ascribed to the dimethyltin cation, $\text{Me}_2\text{Sn}^{2+}$. The observed measurement concentrations of the tri- and di-methyltin species, after various irradiation time are given in Table 4.

Very little is known about the reactions of organotin free radicals in aqueous

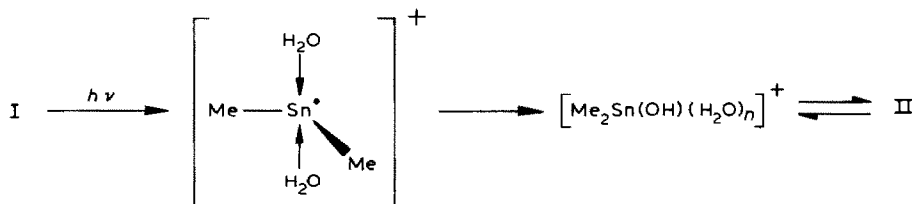
TABLE 4

ANALYTICAL RESULTS, BY ^1H NMR, OF THE UV DEGRADATION OF Me_3SnCl (0.05 *M* IN WATER)

| Irradiation time (h) | <i>N</i> ^a | Me_3Sn^+ | | $\text{Me}_2\text{Sn}^{2+}$ | |
|----------------------|-----------------------|---|--|---|--|
| | | Concentration ^b (<i>M</i> × 10 ⁻²) | Standard deviation ^c (× 10 ⁻²) | Concentration ^b (<i>M</i> × 10 ⁻²) | Standard deviation ^c (× 10 ⁻²) |
| 0 | | 5.0 | — | — | — |
| 5 | 6 | 4.6 | 0.2 | 0.3 | 0.1 |
| 10 | 5 | 4.0 | 0.3 | 0.4 | 0.1 |
| 15 | 5 | 3.3 | 0.2 | 0.5 | 0.1 |
| 20 | 5 | 3.1 | 0.2 | 0.6 | 0.1 |
| 35 | 4 | 2.1 | 0.1 | 1.2 | 0.3 |
| 45 | 2 | 1.8 | 0.1 | 1.6 | 0.1 |
| 65 | 5 | 1.6 | 0.1 | 1.7 | 0.1 |
| 80 | 4 | 0.7 | 0.1 | 1.8 | 0.1 |
| 90 | 5 | 0.5 | 0.1 | 1.8 | 0.1 |
| 110 | 3 | 0.3 | 0.1 | 1.7 | 0.1 |
| 120 | 3 | 0.3 | 0.1 | 1.6 | 0.1 |

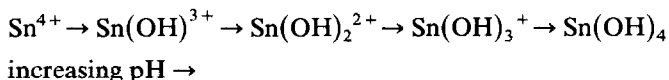
^a Number of samples irradiated. ^b The figure reported is the mean value obtained from *N* irradiated samples. ^c The standard deviation of the concentration is calculated for *N* - 1 samples.

solution, but if it is assumed that cleavage of a Sn–C bond by UV light produces an organotin radical, it is likely that it would react with a water molecule, possibly, in the case of the hydrated cations, with one of the coordinated water molecules. It is known [10] that the species $\text{Me}_2\text{Sn}^{2+}$ and $\text{Me}_2\text{Sn}(\text{OH})^+$ are in equilibrium in aqueous solution. Therefore, reaction of an organotin radical in water probably leads to the formation of a Sn–OH bond



No features were seen in any of the NMR spectra of the irradiated aqueous solutions of Me_3SnCl which could be attributed to the presence of a monomethyltin derivative. Therefore, the irradiated solutions were qualitatively investigated by paper chromatography, but, although this revealed the presence of both dimethyltin and inorganic tin species as degradation products, no monomethyltin compounds were detected. Hence, it is inferred that such species do not accumulate in the UV degradation of the trimethyltin cation in water. This is in contrast to observations by Soderquist and Crosby [15], who, in a study of the UV breakdown of aqueous triphenyltin hydroxide, found that a polymeric monophenyltin compound of the type $(\text{PhSnO}_x\text{H}_y)_z$ was produced.

Elemental analysis of the white precipitate formed during irradiation and its Mössbauer spectrum, which showed a single broad line (δ 0.02 mm s^{-1} ; ΔE_Q 0.00 mm s^{-1} , Lit. δ 0.00 mm s^{-1} , $\Delta E_Q = 0.00 \text{ mm s}^{-1}$ [16]), revealed that the compound was a hydrated form of SnO_2 . The end product of the degradation process, in which organotin radicals react with water to form Sn–OH bonded species, might be expected to be $\text{Sn}(\text{OH})_4$, which would presumably be in equilibrium with other hydroxy species:



The hydrated Sn^{4+} cation is known to be present in aqueous solution only at pH < 1, and at the pH of the irradiated solutions (pH 2–3) $\text{Sn}(\text{OH})_4$ should be present [17]. However, there is no direct evidence for the existence of $\text{Sn}(\text{OH})_4$ in the solid state and it is known that Sn^{4+} precipitates out of aqueous solution as a hydrated form of SnO_2 [18]. By dehydrating and weighing the SnO_2 produced, it was found that the number of moles of inorganic tin species present accounted for the difference between the sum of the concentrations of the di- and tri-methyltin compounds and the total tin molarity (0.05 M), thereby providing further evidence for the absence of a monomethyltin derivative. Therefore, the molarity of the inorganic tin species produced after a given irradiation time was calculated by difference (as for the study in carbon tetrachloride) and Fig. 3 shows a plot of the UV degradation of a 0.05 M aqueous solution of trimethyltin chloride, using the irradiation conditions stated previously.

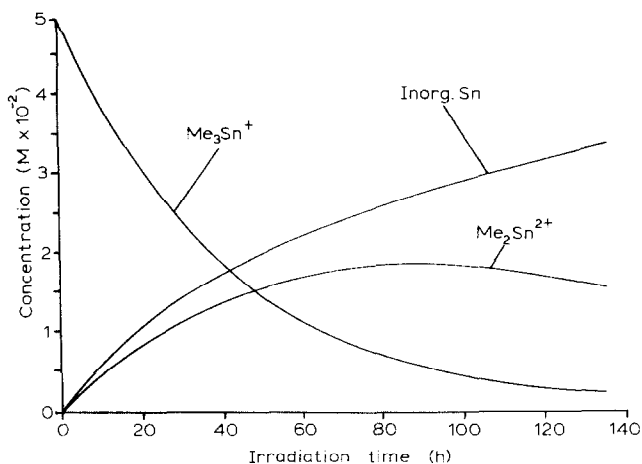
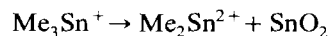


Fig. 3. The UV degradation of 0.05 *M* trimethyltin chloride in water.

In order to establish the relative rates of breakdown of the methyltin chlorides in water, two 0.05 *M* solutions each of (a) Me_3SnCl , (b) Me_2SnCl_2 and (c) MeSnCl_3 were irradiated simultaneously (irradiation intensity: 200–300 nm = 1 mwatt cm^{-2} ; 300–400 nm = 6 mwatts cm^{-2}). At this intensity, the concentration of Me_3Sn^+ in the trimethyltin chloride solution, reached 0.025 *M* after 60 h. The Me_2SnCl_2 solution degraded, forming a precipitate of SnO_2 , but again no monomethyltin compound was detected. After 110 h irradiation, approximately 20% of the $\text{Me}_2\text{Sn}^{2+}$ species had broken down, and hence it was estimated that the time taken for the concentration to reach 0.025 *M* would have been 300 h, this breakdown rate being five times slower than that of Me_3Sn^+ . The MeSnCl_3 solution was found to degrade at an even slower rate, and to obtain quantitative measurements would have involved very long irradiation times, which were not possible because of a slow change in the UV source emission intensity. However, a precipitate of SnO_2 was again produced, and this first became visible after 30 h irradiation. With the Me_2SnCl_2 solution, the SnO_2 precipitate was visible after 6 h irradiation. Therefore, it may be estimated that the breakdown in the MeSnCl_3 solution is approximately five times slower than that in the Me_2SnCl_2 solution.

The presence of dissolved oxygen in the solutions had no effect on the products formed or on the rates of reaction, since identical results were obtained for the breakdown of the tri-, di-, and mono-methyltin compounds when the samples were irradiated (a) in degassed solutions under argon and (b) in solutions open to the air.

From the results it might at first sight be thought that the breakdown of the trimethyltin cation is simply:



However, this reaction would not generate the results shown in Fig. 3, since the concentration of the dimethyltin species is far too low in the initial stages of the procedure and the concentration of the inorganic tin derivative is correspondingly too high. In a flash photolysis study of tetraethyltin and tetravinyltin, Christianson

et al. [19] found that absorption of light of wavelengths between 190–240 nm led to the simultaneous cleavage of two Sn–C bonds, producing a diethyl- or divinyl-tin derivative respectively, and it is possible that a similar process operates for some of the trimethyltin cations in the present case. This would lead to the formation of a monomethyltin species, but, since these were not detected, it must be concluded that further degradation was occurring, the rate of breakdown being comparable to or faster than the rate of formation. The precise form of this proposed monomethyltin compound cannot be positively determined from the available information, but it is unlikely to be the species which is present in a 0.05 *M* aqueous solution of MeSnCl₃, since this was shown to have a very slow breakdown rate. Cleavage of two Sn–C bonds in a trimethyltin compound would presumably produce a monomethyltin diradical, and one possibility is that the spins of the two free electrons could become paired, resulting in the formation of a tin(II) compound, i.e. MeSnX. Since two Sn–Me bonds appear to be broken simultaneously for some of the trimethyltin cations, a similar process could take place with the dimethyltin cation.

Attempts to identify the non-tin containing products of the degradation reactions by irradiating samples in sealed NMR tubes and then recording the ¹H NMR spectrum were unsuccessful, due to the formation of the SnO₂ precipitate, which resulted in broadened signals, and consequent reduction in the signal-to-noise ratio. ¹H NMR spectra recorded from samples which had been centrifuged, to remove the SnO₂, revealed the presence of only a small amount of methanol, but the concentration was far too low to account for all the methyl groups produced by the organotin degradation. Hence, the major non-tin containing products are likely to be gaseous, e.g. methane and ethane, and were not observed because solubilities in water are below the limit of detection of the NMR instrument.

These studies of the breakdown of the methyltin chlorides in carbon tetrachloride and in water have provided further evidence that organotins degrade to inorganic tin species under the influence of UV light. However, the irradiations involved wavelengths as low as 200 nm, whereas in the natural environment the light from the sun reaching the earth's surface consists mainly of wavelengths above 290 nm [20]. Therefore, solutions of the methyltin chlorides in both carbon tetrachloride and water were irradiated behind a glass plate, which cut out all light below 300 nm, and, although a quantitative study was not undertaken, it was qualitatively demonstrated that breakdown did occur, and the same degradation products were identified. Obviously, the breakdown was very much slower, but the important factor is that it did occur.

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