DEGRADATION, SPECTROFLUORESCENCE AND N.M.R. STUDIES OF ORGANOTIN COMPOUNDS.

A Thesis submitted for the Degree of
Doctor of Philosophy in the Faculty
of Science of the University of London

by

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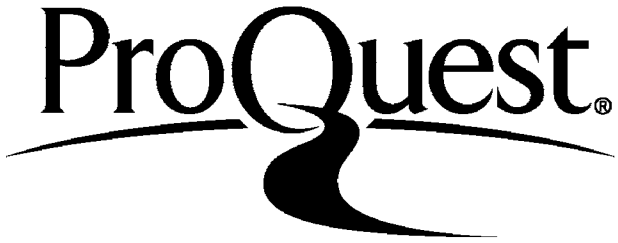

ABSTRACT

Organotin compounds have a very wide range of industrial applications, although R_3SnX species can be toxic to some forms of life. Consequently, it is important to demonstrate that R_3SnX compounds will not accumulate in the environment, but will degrade to non-toxic inorganic forms of tin.

Chapter 1, therefore, reviews the toxicological properties and industrial applications of organotin compounds. The spectroscopic techniques used in the titled studies, mainly N.M.R., are also described.

The methods by which degradation of an organotin compound may occur are discussed in Chapter 2, and the U.V. breakdown of the methyltin and butyltin chlorides, R_nSnCl_{4-n} where R = Me or Bu and n = 1-3, and the U.V. breakdown of the trimethyltin cation, $\{Me_3Sn(H_2O)_2\}^+$, in water are demonstrated. The presence of the hydrated tributyltin cation, $\{Bu_3Sn(H_2O)_2\}^+$, in an aqueous solution of tributyltin ethanesulphonate, Bu_3SnO_3SEt, and the various hydrated monomethyltin species in aqueous solutions of methyltin trichloride are also established.

Chapter 3 reviews spectrofluorescent methods for determining inorganic and organic tin compounds at sub-p.p.m. levels. Fluorescent methods for determining the concentration of triphenyltin species and the total organotin species present in water are developed. A series of new organotin derivatives of the fluorescent reagent, 3-hydroxyflavone, is prepared and their structures in the solid state and in solution are described.

In Chapter 4, the results of a multi-nuclear N.M.R. investigation of a second group of organotin derivatives of hydroxy compounds - the di- and tri-butylstannyl ethers of carbohydrates - are discussed. ^{119}Sn and ^{13}C chemical shifts, $J(^{119}Sn\text{-}O\text{-}^{13}C)$ coupling constants and, spin-lattice relaxation times are reported. The wide range of information obtained from such a study is demonstrated.

THIS THESIS IS DEDICATED TO

MY MOTHER AND FATHER, FOR

THEIR HELP AND ENCOURAGEMENT

THROUGHOUT MY EDUCATION.

ACKNOWLEDGEMENTS

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PUBLICATIONS

The preparation of some water soluble tributyltin biocides.

S.J. Blunden, A.H. Chapman, A.J. Crowe and P.J. Smith
Int. Pest Contr., 1978, July/Aug., 5.

Fluorimetric determination of triphenyltin compounds in water.

S.J. Blunden and A.H. Chapman
Analyst, 1978, 103, 1266.

Multi-nuclear (^{119}, ^{13}C, ^{1}H) Fourier transform N.M.R. studies of di- and tri-butylstannyl ethers of carbohydrates.

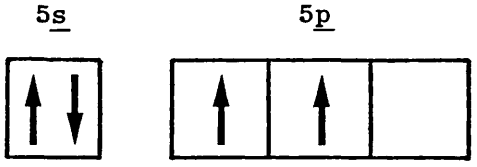
S.J. Blunden, P.J. Smith, P.J. Beynon and D.G. Gillies
Carbohydr. Res., 1981, 88, 9.

CHAPTER 1

INTRODUCTION

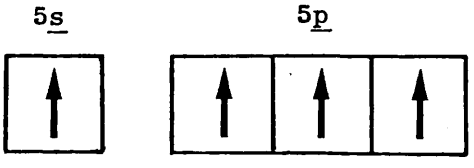
1.1 General considerations of bonding.

Tin, an element of Group IV, together with carbon, silicon, germanium and lead has the outer electronic configuration, $5s^2\ 5p^2$.



The inner shells are completely filled, and, therefore, no bond formation involving the use of the inner orbitals is possible.

Tin, like germanium and lead, with an $s^2\ p^2$ outer electron configuration, can form compounds in both the +4 and +2 oxidation states, depending upon the way in which the valence electrons are used for bonding. If the two 5s electrons remain as an inert, non-bonding pair, as illustrated above, the oxidation state is +2, whereas promotion of one of the 5s electrons to the vacant 5p orbital produces an electronic configuration characteristic of the +4 oxidation state:

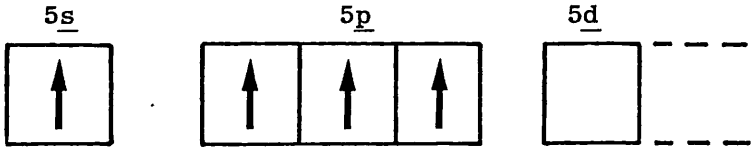


In contrast to carbon, tin does not form $p_\pi - p_\pi$ multiple bonds and bonding in tin compounds is, therefore, exclusively of a single covalent or ionic nature.

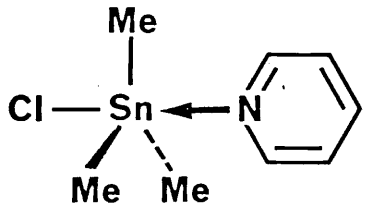
1.1.1 Tin(IV) compounds.

The simplest bonding situation which can occur in tin(IV) compounds results from promotion of one of the 5s electrons to the empty 5p orbital, forming an sp^3 hybrid. This arrangement produces tetrahedrally orientated bonds and a coordination number of four. Stannic chloride and the tetraorganotins, along with many other tin compounds, have this structure.

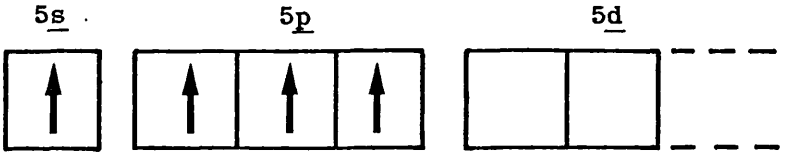
The coordination number of the tin atom can be increased by making use of the empty energetically favourable 5d orbitals in the bonding. Thus, dative covalent bonds may be formed by the overlapping of empty hybrid orbitals on the metal with filled orbitals on a suitable ligand. For example, pentacoordination is associated with sp^3d hybridisation,



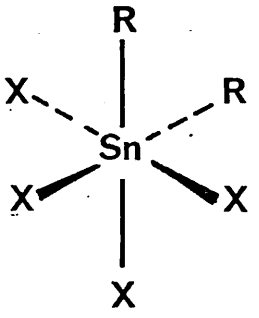
giving rise to a trigonal bipyramidal structure. The tetraorganotin compounds, R_4Sn, show no tendency to increase their coordination number owing to the tin atom having a very weak Lewis acidity due to it being surrounded by four electron-releasing alkyl groups. However, replacement of one of the organic groups by an electronegative atom or ligand increases the ability of the tin atom to act as an electron acceptor. For example, trimethyltin chloride is known to form[1] a 1:1 adduct with pyridine, and this has a trigonal bipyramidal tin atom geometry, with equatorial methyl groups, as shown below:



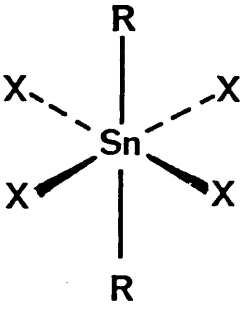
Hexacoordination is usually associated with sp^3 d^2 hybridisation, the shape of the molecule being octahedral.



In triorganotin compounds the tin atom is only a weak electron acceptor and consequently these compounds prefer to increase their coordination number to five. In contrast, diorganotin compounds of the type R_2SnX_2 show a strong tendency to increase their coordination number to six by accepting two monodentate donor molecules (or one bidentate ligand). The configuration of the organic groups in the resulting octahedral complexes may be cis- or trans-, as shown below.



cis-

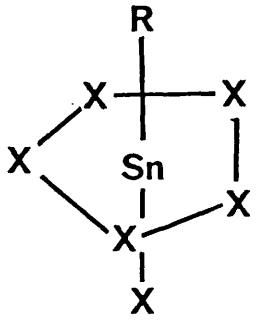


trans-

The cis-octahedral configuration is usually found to be sterically favourable when two bidentate ligands are present, e.g. dimethylbis(8-quinolinoxy)tin(IV), $Me_2Sn(C_9H_7NO_2)_2$[2], but if one or both of these bidentate ligands is replaced by monodentate groups, the trans- isomer usually results, e.g. dimethyl bis(pyridine-N-oxy)tin dichloride, Me_2SnCl_2, 2pyO[3].

Although coordination numbers of five and six are by far the most abundant for tin(IV) compounds, a few examples of higher coordination number are known. If three of the tin atom's 5d orbitals are combined with the 5s and three 5p orbitals, the resulting sp^3 d^3 hybridisation could give rise to seven coordinate tin contained in a pentagonal

bipyramidal geometry:

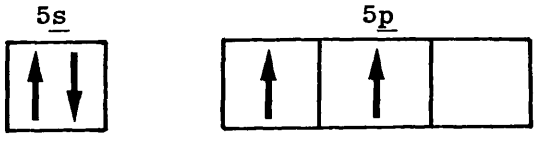


Examples of this structure are found in $MeSn(NO_3)_3$[4] and $MeSn(SCSNEt_2)_3$[5].

Two inorganic tin(IV) compounds containing an unusual eight coordinate metal atom are stannic nitrate[6] and stannic phthalocyanine[7]. The former consists of molecular $Sn(NO_3)_4$ units with the four bidentate nitrate groups symmetrically bonded to the tin atom; the eight oxygen atoms form a dodecahedral arrangement around the metal. In the latter compound, the tin atom occupies the centre of a square antiprism, formed by two squares of four nitrogen atoms (from each phthalocyanine ring), displaced by about 42^0 from each other; the tin atom being equidistant from each of the eight nitrogens.

1.1.2 Tin(II) compounds.

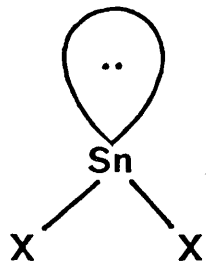
The ground state electronic configuration of tin in its +2 oxidation state consists of a completely filled 5s orbital and two half-filled 5p orbitals:



Thus, the element may form derivatives in the following ways:-

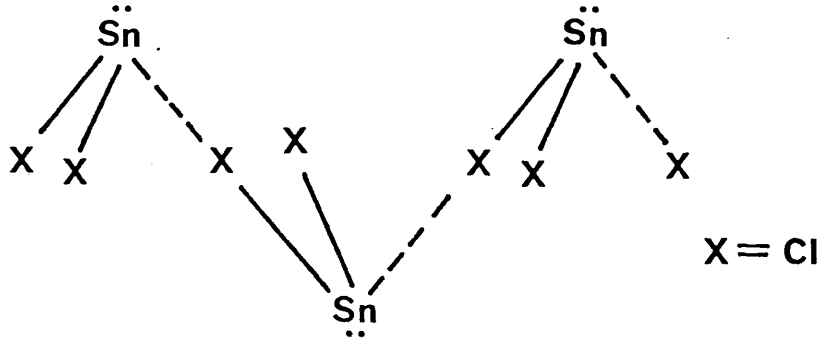
A) by loss of the two 5p electrons, forming the stannous ion, Sn^{2+}.

B) by use of the two 5p electrons in covalent bond formation, by invoking sp^2 hybridisation, where the lone pair is sterically active.

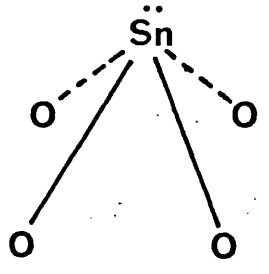


Tin(II), chloride and bromide have been shown[8] by electron diffraction studies to be of this structure in the vapour phase.

C) the tin(II) atom shows a marked tendency to use all of its three 5p orbitals for bonding. Thus, the empty 5p orbital may be used as an acceptor, leading to a three coordinate pyramidal structure, e.g. $CsSnCl_3$[9], which is widely found in tin(II) compounds Stannous chloride[10] in the solid state adopts a chain structure involving bridging halogen atoms to complete this pyramidal geometry.



The 5d orbitals are well removed energetically from the 5s-orbital. However, hybridisation involving 5d orbitals has been known to occur with the formation of a square pyramidal sp^3d hybrid e.g. stannous oxide[11].



D) bonding may also occur by overlap of the lone pair 5s orbital with an empty orbital on an acceptor species, e.g. $\{Ph_3PMe\}_3^{+}\{Pt^{II}(SnCl_3)_5\}^{3-}$.[12]

1.2. Sn-C and Sn-X bond lengths and bond dissociation energies.

If the covalent radius of a ligand, X, is subtracted from the measured bond length, Sn-X, in a tin compound, it is found, within experimental error that a value of 14 nm. is nearly always obtained. This value is the covalent radius of the tin atom and is surprisingly independent of the nature of the ligand. Table I[13] illustrates some examples of this.

Table I[13]: Sn-C and Sn-X bond lengths and covalent radius of tin.

Bond	Length (nm.)	Measured in	Covalent radius of X (nm.)	Covalent radius of Sn (nm.)
Sn-C	21.8 ± 0.3	Me_4Sn	7.7	14.1 ± 0.3
	21.9 ± 0.3	Me_3SnCl	7.7	14.2 ± 0.3
	21.9 ± 0.3	$MeSnCl_3$	7.7	14.2 ± 0.3
Sn-H	17.0 ± 0.15	$MeSnH_3$	2.8	14.2 ± 0.2
Sn-O	20.8 ± 0.6	Et_3SnOAr	6.6	14.2 ± 0.6
Sn-Cl	23.7 ± 0.3	Me_3SnCl	9.9	13.8 ± 0.3
	23.4 ± 0.3	Me_2SnCl_2	9.9	13.5 ± 0.3
	23.2 ± 0.3	$MeSnCl_3$	9.9	13.3 ± 0.3
	23.0 ± 0.3	$SnCl_4$	9.9	13.1 ± 0.3

A slight decrease in bond length is observed only when there is an accumulation of strongly electronegative ligands around the tin. This trend may be demonstrated by consideration of the Sn-Cl bond lengths in the methyltin chlorides, Me_nSnCl_{4-n}, Table I[13].

The bonding of tin is therefore almost entirely covalent in the majority of organotin compounds, even in those with tin-halogen bonds. The polarity which would be expected to occur due to the difference in electronegativities is not observed, possibly because of the relatively large bond lengths. For the same reason bonds are found to be easily polarisable, and will undergo ionic dissociation especially in polar coordinating solvents, L.

$$R_3SnX + 2L \rightleftharpoons (R_3SnL_2)^+ + X^-$$

Long bonds may generally be said to have low strength and also make the central atom more vulnerable to the approach of other species. The increased bond length in tin compounds compared to similar C-, Si- and Ge- analogues is, thus, the reason for the increased reactivity and decreased thermal stability. This is illustrated by comparing some average bond lengths and bond dissociation energies for the Group IV elements, Table II[13].

Table II[13]: Average bond lengths and bond dissociation energies for element-carbon bonds of the Group IV tetraalkyls.

	C-C	C-Si	C-Ge	C-Sn	C-Pb
bond length (nm.)	15.4	19.4	19.9	21.7	22.9
bond dissociation energy (kcals mol^{-1})	87	70	60	50	31–37

Bond dissociation energies are naturally dependent upon the nature of the particular groups concerned. Therefore, some mean bond dissociation energies for specific groups bonded to tin are given in Table III[14].

Table III[14]: Mean bond dissociation energies, $\overline{D}$, for some Sn-C bonds.

Bond	$\overline{D}$ (kcals mol^{-1})
Sn-Me	52.1
Sn-Et	46.2
Sn-Pr	47.2
Sn-Bu	46.7
Sn-Ph	61.4

Mean bond dissociation energies although being useful for indicating trends, are imperfect guides for reactivity, since, by definition, they are only average values, i.e. $\overline{D}$ (Sn-Me) is one quarter of the total energy required to break four Sn-C bonds in Me_4Sn. This value is different from the bond dissociation energy which is the energy required to break just one Sn-Me bond. Also mean bond dissociation energies refer

to homolytic bond fission, whereas the majority of reactions refer to heterolytic cleavage. As an example of the differences involved, it has been shown[15] that in dimethyltin dichloride 56 kcals mol^{-1} are required to break the first Sn-C bond, whereas only 32 kcals mol^{-1} are required to break the second.

1.3. Toxicology of organotin compounds.

Tin metal and its inorganic salts are generally considered to be non-toxic, the metal probably being non-ionised at physiological pH, and the oxides being non-reactive. However, organotin compounds exhibit a wide range of toxicological properties, which are very much dependent upon the number and type of organic groups attached to the metal atom.

Progressive introduction of organic groups, R, in any R_nSnX_{4-n} series produces a maximum biological activity when n = 3, as illustrated in Figure I(a). It is also found that if the n-alkyl chain length is increased within any R_3SnX series, the highest mammalian toxicity is attained for the triethyltin compounds. For insects, however, the trimethyltins are usually most active, whereas for Gram-negative bacteria it is the tri-n-propyltins which show most activity and for Gram-positive bacteria and fungi it is the tri-n-butyltins. Further increase in the alkyl chain length beyond that of maximum toxicological effect produces a sharp drop in the biological activity and the tri-n-octyltin compounds are considered to be essentially non-toxic to all living species. These toxicological trends are shown in Figures I(b) and II. Of the other classes of organotin compounds, triphenyltins show a high fungicidal activity, whilst the tricyclohexyl- and trineophyl-tin derivatives are active acaricides. In general, variation of the inorganic radical, X, within any R_3SnX series, has very little effect upon the biological activity, unless, of course, X is itself biologically active, in which case the activity of the compound may be enhanced.

The lower tetraalkyltin compounds show a delayed toxic action in mammals due to the *in vivo* formation of the more toxic R_3SnX derivative[16].

FIGURE I

a) The relative toxicological activity of R_nSnCl_{4-n} (n = 0-4) to houseflies (R = Ph) and fungi (R = Et).

b) The toxicological activity to rats and fungi of $R_3SnO.CO.Me$ with an increasing number of carbon atoms in the R chain.

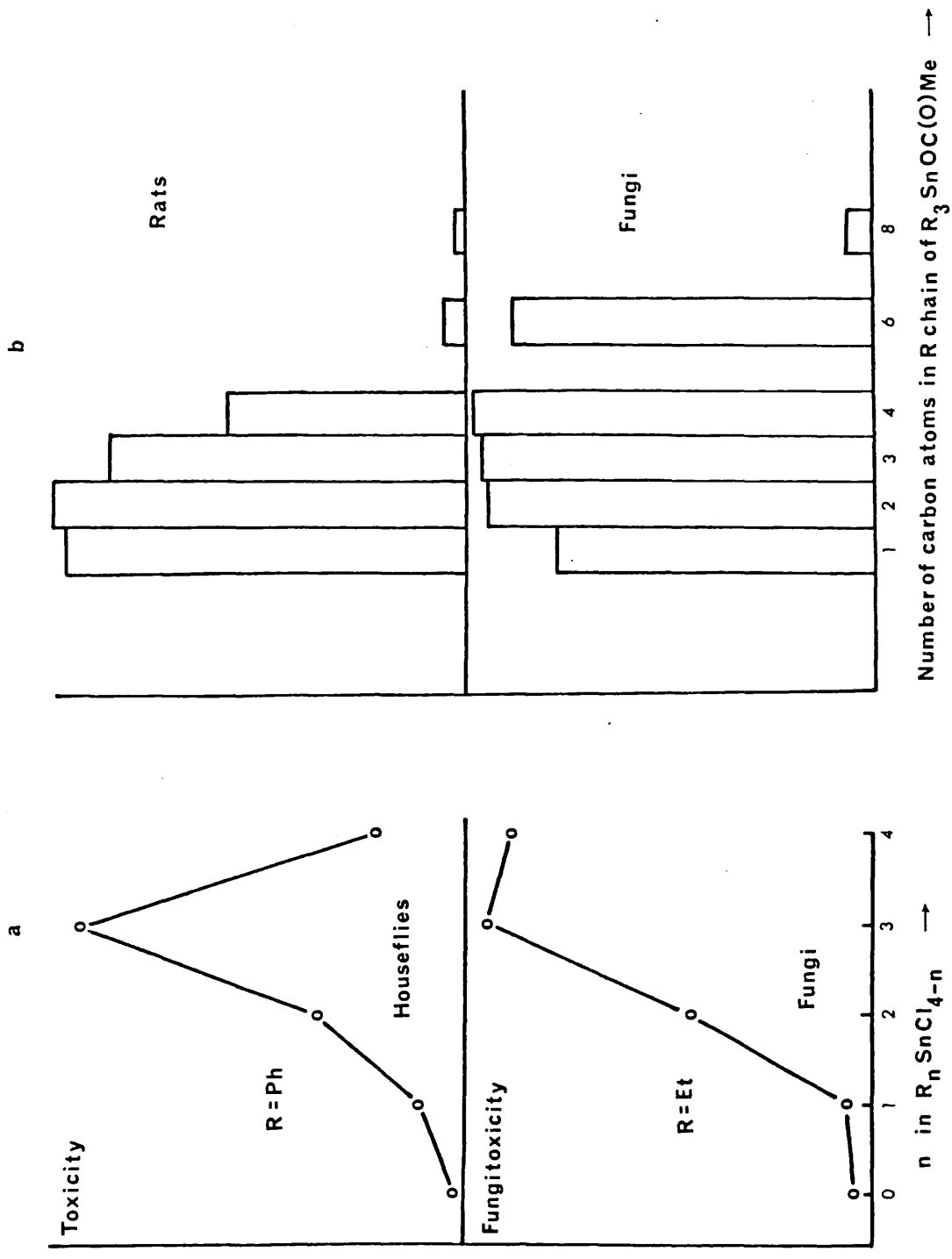
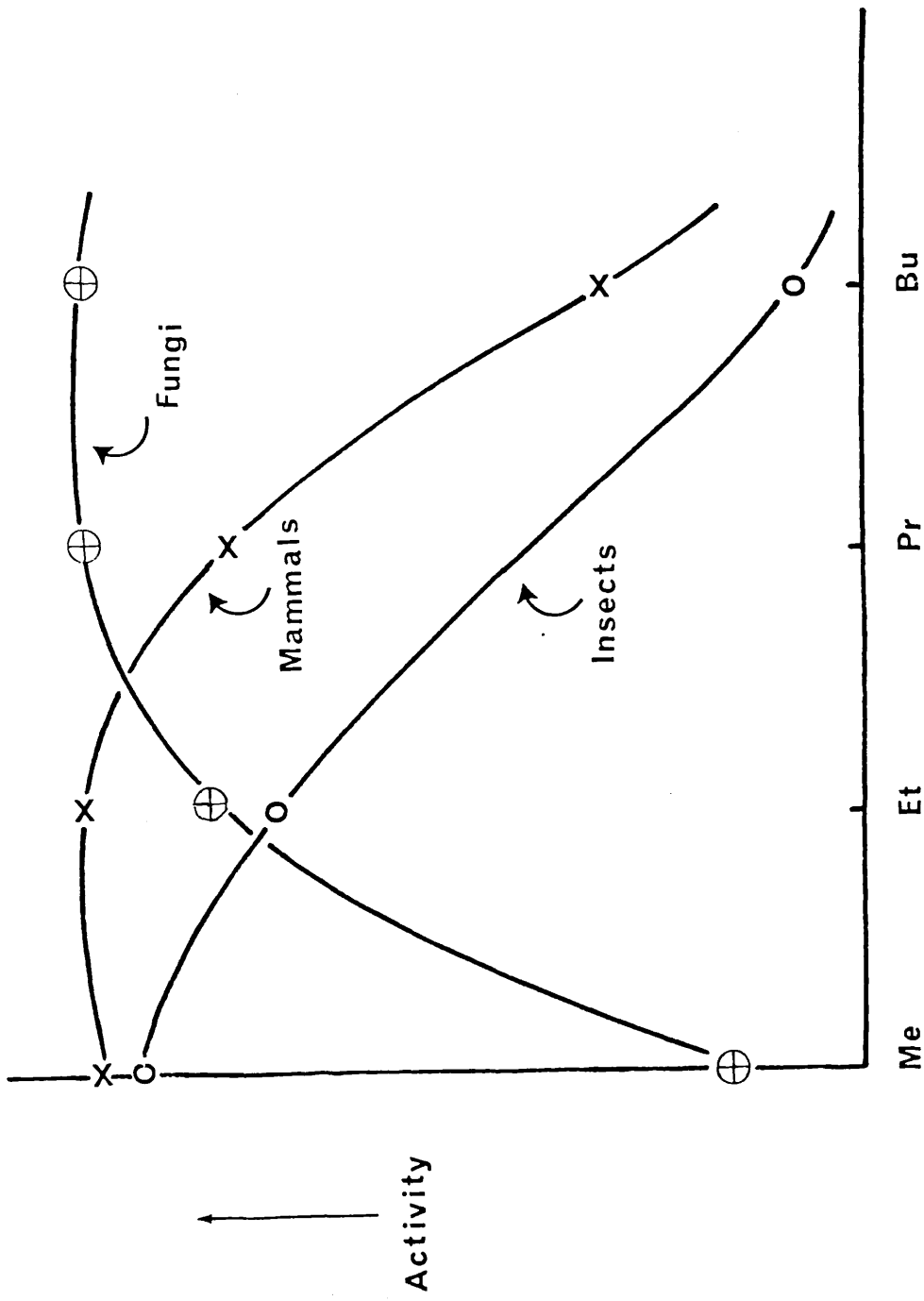

a
Toxicity
R = Ph
Houseflies
Fungitoxicity
R = Et
Fungi
0
1
2
3
4
n in R_nSnCl_{4-n} →
b
Rats
Fungi
1
2
3
4
6
8
Number of carbon atoms in R chain of $R_3SnOC(O)Me$ →

FIGURE II

The relative toxicological activity to fungi, insects and mammals of $R_3SnO.CO.Me$ (R = Me, Et, Pr and Bu).


Fungi
Mammals
Insects
Activity
Me
Et
Pr
Bu
R in $R_3SnO.CO.Me$

Decreasing toxicity with increasing alkyl chain length is also found to occur in the di-n-alkyl- and mono-n-alkyltin compounds. The latter, however, do not appear to have any important toxic action in mammals[17].

An extensive survey has recently been carried out on organotin toxicological data by Smith[18].

1.4. Industrial uses of organotins.

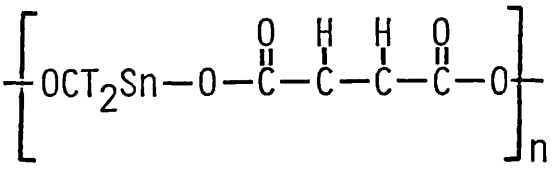
1.4.1. P.V.C. stabilisers.

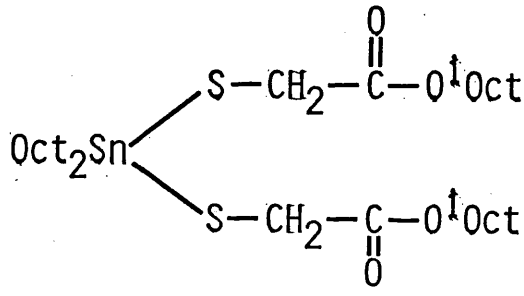
Polyvinyl chloride (P.V.C.) has a tendency to degrade upon heating (during processing at 180-200^{0}C) or on prolonged exposure to light, leading to a yellowing of the plastic and severe embrittlement. This is due to the loss of HCl from the polymer. It was found that the addition of certain chemicals to the P.V.C. before processing could inhibit this breakdown and protect it during its service life. In fact, some of the most effective P.V.C. stabilisers known are the mono- and di-alkyltins, and this use provides the largest single application of all organotin compounds (ca. 20,000 tons of chemicals worldwide). The high price of the organotin stabiliser is offset by the excellent long-term transparency conferred to the plastic[19].

Organotin stabilisers fall into two groups - those compounds containing Sn-S bonds, which are used as heat stabilisers and those containing Sn-O bonds which are used as light stabilisers.

The low toxicity of the dioctyltin compounds has allowed their use as stabilisers in food-contact P.V.C.. Two such compounds in commercial use are di-n-octyltin cis- butane-dioate polymer, (1) and di-n-octyltin-S,S´-bis-(iso-octyl mercaptoethanoate), (2),

(1)



(2) 

while the dimethyltin analogue of (2) has been accepted as a heat stabilizer for P.V.C. potable water piping in the U.S.A.[20].

The effectiveness of organotin stabilizers is believed to be due to the following reasons:

i) they inhibit dehydrochlorination, by exchanging their anionic groups, X, with reactive chlorine sites in the polymer.
ii) they scavenge the hydrogen chloride which is produced and which would induce further elimination.
iii) they produce the compound HX, and so may help to inhibit other side reactions.
iv) they act as antioxidants, and so prevent breakdown by atmospheric oxygen.

1.4.2. Catalysts and curing agents[21].

A number of dialkyltins are used for the room-temperature vulcanisation of silicones. The three most commonly used derivatives are dibutyltin diethanoate, dibutyltin di-(2-ethyl-hexanoate) and dibutyltin dilaurate. Room-temperature addition of the organotin catalyst to the liquid silicone oligomer brings about cross-linking of the silicone, due to the reactive carboxylate groups, and produces a flexible elastomeric solid.

These same dibutyltin compounds are also used commercially to catalyse the addition of alcohols to isocyanates producing polyurethanes[22].

1.4.3. Preservation of materials.

Since the work of van der Kerk and Luijten[23], proposing the use of organotin compounds as biocides in wood preservation, a number of formulations have become commercially available, of which the most effective fungicidal constituent is bis(tri-n-butyltin) oxide, TBTO. Tris(tributyltin) phosphate and naphthenate are also used in some countries.

One disadvantage of the tributyltin wood preservatives is their low aqueous solubility and they must, therefore, be applied in organic solvents, which increases the application costs and also may constitute a fire hazard. One method at present of overcoming this problem is to apply the organotin in an aqueous dispersion with a suitable quaternary ammonium salt, $R_4N^+X^-$;[24] the quaternary ammonium cation perhaps having the ability to stabilise the tributyltin anion, $Bu_3SnX_2^-$ [25], in aqueous solution. An aqueous formulation of this type has recently been introduced in Sweden for wood protection.

1.4.4. Antifouling.

The attack of timber-hulled boats by marine boring creatures such as the Teredo worm, and the attachment of barnacles and other organisms to all types of hulls can seriously impede the running of the vessel.

The use of paints containing triorganotin compounds[26], particularly the tributyl- and triphenyl-tin derivatives has been found to be very effective in eliminating this fouling problem.

By incorporation of the organotin into a polymer matrix, the active lifetime of the antifouling paint may be considerably extended. In this way, the toxic agent is slowly released from the hull into the water and effectively kills off adjacent marine life. Examples of such polymer matrices are poly(tributyltin methacrylate), and poly(tributyltin 2-methylpropenoate); additionally triorganotins have been incorporated into chloroprene rubbers[27,28].

Tributyltin impregnated rubber has also been found to be of valuable use in combating the water-borne tropical disease of Schistosomiasis by destroying the intermediate hosts - certain species of snails.

1.4.5. Organotins in agriculture.

Triphenyltin acetate and triphenyltin hydroxide[29] have for many years been used for the control of a wide variety of fungal diseases, particularly the potato blight fungus, Phytophthora infestans. While, tricyclohexyltin hydroxide[30,31], 1-tricyclohexyltin 1,2,4-triazole[32] and bis(trineophyltin) oxide[33] are all effective acaricides for the control of plant feeding mites. Tributyltin compounds are not used in agriculture due to their high phytotoxicity.

In general, the advantages of organotin agrochemicals include their low phytotoxicity, their selective activity to the target organism and their non-persistence in the environment, in that they degrade to a non-toxic species.

1.4.6. Miscellaneous uses of organotins.

Some diorganotin compounds have been used as anthelmintics in fish[34] and poultry[29], particularly dibutyltin dilaurate.

Certain tributyltin compounds have been used as fungicides in cellulose paints and pastes[35], and in P.V.C. films[36]. Some have been formulated into disinfectant sprays, waxes and polishes for use in hospitals[37] and tributyltin chloride has been suggested as a rodent repellent[38].

In Japan, dimethyltin dichloride is being used as an alternative to stannic chloride for coating glass with a thin film of stannic oxide[39]. The organotin vapour is brought into contact with the hot glass surface (at 500-1000^{0}C), where decomposition and oxidation occurs. This treatment renders the glass scratch resistant, lustrous or electroconductive, depending upon the thickness of the SnO_2 film deposited. Tetramethyltin[40] and dibutyltin diacetate[41] have also been suggested for this purpose. Diorganotin borates[42] and tetraalkyltin compounds[43] have been used as high temperature stabilisers and antioxidants for lubricating oils. Monoorganotin compounds[44] and fluoroalkyltins[45] have been patented as water-proofing agents, and triorganotin phosphates, sulphonates and carboxylates have been proposed as antistatic treatments[46].

1.5. Physical measurements

1.5.1. Nuclear magnetic resonance (N.M.R.) spectroscopy

1.5.1.1. Basic techniques

Many nuclei possess quantised spin angular momentum which is characterised by the quantum number, I, and nuclei with both odd mass and odd atomic number have the value $I = \frac{1}{2}$. Associated with the nuclear spin is a magnetic moment, μ, which is colinear with it. The magnetic moment interacts with an applied magnetic field, B_o, along the z direction, with an energy

$$E = -\mu_z B_o$$

Since μ_z is quantised with $2I + 1$ states, there are $2I + 1$ energy levels, their separation, ΔE, given by

$$\Delta E = \frac{\mu_z B_o \hbar}{I}$$

$$= \gamma B_o \hbar$$

where γ is the magnetogyric ratio and $\hbar$ is Planck's constant divided by 2π. Thus, to induce transitions between the energy levels, electromagnetic radiation of the appropriate frequency, ν,

$$\nu = \frac{\Delta E}{\hbar}$$

must be applied, leading to the resonance condition

$$\nu = \frac{\gamma}{2\pi} B_o$$

or $$\omega = \gamma B_o$$

where ω = angular frequency in rad. $sec.^{-1}$

In fact, the magnetic moment precesses about B_o at the Larmor frequency.

In continuous wave (CW) N.M.R. the spectrum may be generated by sweeping either the magnetic field or the frequency. Nuclear magnetic moments are very weak, and, hence, the frequency of the radiation is low and is in the radio frequency (RF) region. The CW method is technically simple, but essentially only one frequency can be excited at a time, and a disadvantage is that time is spent searching in regions where there is no signal. The technique is most successful for studying sensitive nuclei such as hydrogen, fluorine and phosphorus. The sensitivity may be improved by storing repetitive scans on a CAT (Computer Averaging of Transients). The improvement in the signal-to-noise (S/N) ratio obtained is proportional to the square-root of the number of scans, but it is still insufficient for convenient observation of many less sensitive nuclei.

It is obvious that a saving in time, and, thus, an increase in sensitivity would be obtained if all resonance frequencies were excited simultaneously. This may be achieved by irradiation with a short burst (pulse) of RF energy. A pulse of RF, lasting τ_p seconds, at a frequency ν_o, excites a usable frequency range given by the expression

$$\nu_o \pm \frac{1}{4\tau_p}$$

and so, for example, a 10μ sec. pulse would excite $\nu_o \pm 25$ kHz.

In discussing pulse methods it is helpful to refer to the motion of the magnetisation not in the fixed coordinate system of the laboratory, but in a system rotating about B_o, in the same direction in which the nuclear moments precess. In this rotating frame of reference, the magnetisation vector of the nucleus, M_o, is stationary and lies along the z' axis, as is the RF field, B_1, along the x' axis (where x', y' and z' refer to the rotating x, y, and z axes). The vector, M_o, is rotated through an angle θ by the action of the RF pulse, according to the equation

$$\theta = \gamma B_1 \tau_p$$

Since γ is constant and so too is the RF field strength, B_1, the angle of rotation, θ, is dependent upon the pulse length, τ_p. If $\theta = 90^0$ the so called '90^0 pulse' is obtained and the magnetisation immediately after the pulse is in the x'y' plane. When the pulse is switched off the magnetisation begins to relax to its equilibrium position, M_o, over a period of time. (Nuclear relaxation times and mechanisms are discussed in Section 1.5.1.4.). The N.M.R. signal is observed along the y' axis and is detected as a decay, termed the free induction decay (FID). This signal is in the time domain, and in all but the simplest of cases is not readily interpretable. However, the usual N.M.R. spectrum in the frequency domain can be obtained by the mathematical relationship of Fourier transformation (FT).

A typical improvement in the signal to noise ratio obtained from pulse methods compared to CW is approximately 10, and, since, the S/N increases as the square root of the time spent. (i.e. No. of pulses) the same S/N may be obtained in one hundredth the time. It would at first appear that sensitivity may be improved by simply increasing the number of pulses within

a given time, i.e. by reducing the delay time between pulses. However, if the relaxation time of the nucleus is long compared to the time between pulses, there may have been relatively little relaxation of the magnetisation vector to its equilibrium position, M_o, and so the following 90^0 pulse will result in a greatly attenuated signal. This problem may be overcome by prolonging the waiting period between pulses, permitting restoration of M to its equilibrium value, but this means that most of the experiment time is spent waiting rather than accumulating data. Thus, in order to obtain a faster pulse rate, a pulse angle, θ, is chosen such that optimum sensitivity is obtained for a given ratio of the pulse delay time to the relaxation time, T_1. This angle is known as the Ernst angle[47].

Although pulse techniques, combined with the use of large samples at high fields, have produced dramatic improvements in sensitivity, N.M.R. is basically an insensitive technique and does not lend itself, as yet, to the study of compounds at the parts per million level, as might be encountered in environmental situations, but at higher concentrations the method has very good applications as a fingerprinting technique and in structural analysis.

1.5.1.2. The chemical shift

The magnetic field experienced by the nucleus is modified by the chemical environment by which it is surrounded. The local magnetic field is given by the expression

$$B_{loc} = B_o (1-\sigma)$$

where σ is the screening constant and may be expressed as the sum of two parts, the diamagnetic term, σ_D, and the paramagnetic term, σ_P.

$$\sigma = \sigma_D + \sigma_P$$

Diamagnetic term, σ_D.

If a nucleus is considered having an s electron, in the applied magnetic field the electron will circulate so as to produce a field opposing that applied. Hence, the field felt at the nucleus is reduced.

Any electronegative group on a molecule which will withdraw electron density will decrease the shielding and the resonance will appear at a lower field. The diamagnetic term is the dominant shielding factor for protons.

The paramagnetic term, σ_P.

The local paramagnetic contribution to the overall screening constant arises from the circulation of electrons in the bonds of the molecule and is the dominant factor for nuclei other than hydrogen. It produces an induced magnetic moment which reinforces the applied field and, therefore, leads to deshielding. The paramagnetic term is difficult to calculate, since it is affected by many factors, but a simplified expression by Jameson and Gutowsky[48] is given below:

$$\sigma_P = - \frac{2e^2\hbar^2}{3m^2c^2\Delta E} \left(\langle r^{-3} \rangle_{np} Q_{np} + \langle r^{-3} \rangle_{nd} Q_{nd} \right)$$

ΔE is the mean electronic excitation energy and determines the extent to which the ground and excited states are mixed by the field.

$\langle r^{-3} \rangle_{np}$ and $\langle r^{-3} \rangle_{nd}$ are the mean inverse cubes of the valence p and d electron-nuclear distances. Since, these quantities

increase with increasing atomic number in a given group of the periodic table[49], it may be seen that ^{119}Sn chemical shifts would be expected to cover a wider range than ^{29}Si or ^{13}C.

Q_{np} and Q_{nd} represent the electron imbalance associated with the valence p and d electrons and depend upon coordination number, hybridisation and the bond ionicity[49].

1.5.1.3. Spin-spin coupling

N.M.R. spectra are often seen to contain more lines than can be accounted for by consideration of the number of different types of equivalent nuclei. This splitting of resonances, termed spin-spin coupling, is due to interactions of the magnetic moments of neighbouring non-equivalent nuclei, and is independent of the applied magnetic field. A group of p equivalent nuclei will split the resonance associated with a neighbouring group into p + 1 lines with intensities given by the pth line of Pascal's triangle.

Coupling can be a valuable aid to structural determination. However, a large amount of splitting will cause a spectrum to appear incredibly complex, and often a simplified decoupled spectrum is preferable. Heteronuclear decoupling may be achieved relatively easily by simultaneously irradiating the sample with the resonance frequency of the nuclei causing splitting. For example, in ^{13}C or ^{119}Sn N.M.R. where each resonance would normally be split into a multiplet by coupling to directly-bonded or near-neighbour protons, coupling may be destroyed by simultaneous irradiation at the frequency of the proton resonances, and the lines collapse to form singlets.

1.5.1.4. Relaxation times and mechanisms.

Section 1.5.1.1. described briefly how the magnetisation vector, M_o, lying along the z' axis may be tipped through an angle, θ, by

the action of an RF pulse, such that a component of M is generated along the y' axis. The system has been displaced from equilibrium and after the pulse is switched off, $M_{y'}$, will return to its equilibrium value of zero, by various relaxation processes.

The exchange of spin energy between nuclei causes the moments to spread out in the x'y' plane. Thus, $M_{y'}$, decays with a time constant, T_2, the spin-spin or transverse relaxation time. $M_{y'}$, is also reduced by the effect of magnetic field inhomogeneity. Since the magnetic field, B_o, is not perfectly homogeneous, nuclei in different parts of the sample experience different magnetic fields and so precess at slightly different frequencies causing $M_{y'}$, to diminish. Therefore, the overall decrease of $M_{y'}$, to zero is characterised by T_2^*. The dissipation of spin-energy to the lattice causes the magnetic moments to tip back towards the z' axis, and this action is characterised by a time constant, T_1, the spin-lattice or longitudinal relaxation time. By the time the moments have tipped back to the z' axis and returned M_z, to M_o, there can be no components in the x'y' plane. Therefore, T_2^* can never be longer than T_1. Thus, in general, we have

$$T_2^* \leq T_2 \leq T_1$$

Since the nucleus can remain in a given energy level no longer than the relaxation time, the minimum width of the N.M.R. line can be estimated from the Heisenberg Uncertainty Principle,

$$\Delta E \, \Delta t \geq h$$

where ΔE and Δt are the uncertainty in energy and time respectively. Therefore, the line width at a half the maximum intensity, $\nu_{\frac{1}{2}}$, is

given by

$$h\,\nu_{\frac{1}{2}}T \geq h \Rightarrow \nu_{\frac{1}{2}} \geq \frac{1}{T}$$

and since the shortest relaxation time is T_2^*, the maximum line width, $\nu_{\frac{1}{2}}$, is better expressed as

$$\nu_{\frac{1}{2}} = \frac{1}{\pi T_2^*}$$

Spin-spin and spin-lattice relaxation occur by the action of the nuclear spin with fluctuating local magnetic fields, generated by individual magnetic moments on molecules as they move about in solution. If the macroscopic magnetisation is perturbed from its equilibrium position, giving components along the x', y' and z' axes, the interaction of the microscopic local fields, b, with M is given by

$$(b \times M) = i(b_{y'} M_{z'} - b_{z'} M_{y'}) + j(b_{z'} M_{x'} - b_{x'} M_{z'}) + k(b_{x'} M_{y'} - b_{y'} M_{x'})$$

Thus, it is apparent that $b_{x'}$ fields provide relaxation for $M_{y'}$ and $M_{z'}$, $b_{y'}$ for $M_{z'}$ and $M_{x'}$, and $b_{z'}$ for $M_{x'}$ and $M_{y'}$. Consequently, fluctuating magnetic fields with components in the x' and y' directions are efficient for relaxing spin-lattice (T_1) and spin-spin (T_2) processes, while fields with components in z' are efficient for T_2 only.

A static component of b in the z' direction (rotating frame) is static in the laboratory frame also and so gives a zero frequency contribution to T_2. However, a static component of b in the x' or y' direction corresponds to a high frequency (ω_o) component of b in the laboratory frame, so only high frequencies (of the order of the resonance frequency) affect T_1. Thus, if

the microscopic fields have components at the appropriate frequencies they can cause relaxation, and the larger the components are, the more efficient is the relaxation and the shorter are the relaxation times. For spin-lattice relaxation the relevant range of frequencies are in the MHz region, and so motions important for relxation are rotation and diffusion, while electronic and vibrational motions occur on much shorter timescales and are therefore unimportant. The motions of rotation and diffusion may be described by a parameter, τ_c, the correlation time. For translational motion, τ_c is the average time between molecular collisions and for rotational motion it is the average time for the molecule to rotate one radian.

Spin-lattice relaxation may result from a number of different mechanisms:-

A) Dipole-dipole relaxation.

B) Spin-rotation relaxation.

C) Chemical shift anisotropy.

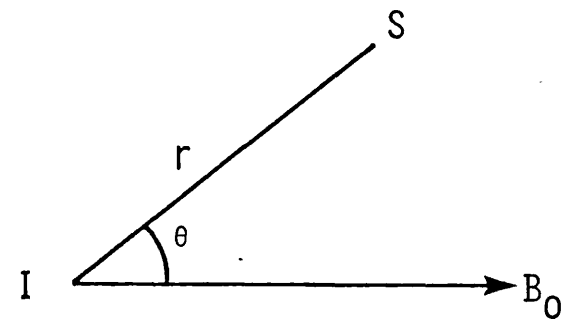
D) Scalar relaxation.

E) Quadrupole relaxation.

F) Electron-nuclear relaxation.

A) Dipole-dipole relaxation.

This is probably the most important relaxation mechanism for spin $\frac{1}{2}$ nuclei in the liquid state. Consider two nuclei in the same molecule, I and S. If the molecule is stationary, the total magnetic field, B_t, experienced by I will have two contributions, the applied field, B_o, and a second local field, B_{loc}, resulting from S. The strength of the interaction of the two magnetic moments, μ_I, μ_S, depends upon their separation, r, and the relative orientation, θ.



The local field at I due to S is given by the expression

$$B_{loc} = \pm \frac{\mu_s}{r^3} (3\cos^2\theta - 1) = \frac{\gamma_s I_s \hbar}{r^3} (3\cos^2\theta - 1)$$

The ± sign arises, since depending upon the spin-state of the nucleus, S, the local field may add to or subtract from the contribution from the applied field, B_o. As the molecule moves about, θ becomes a time dependent function. If the motion is fast enough the local field averages to zero, however, more important is that since θ is time dependent, the local magnetic fields fluctuate in time and a potential relaxation mechanism is generated. The relaxation rate, R, is equal to T^{-1}, and it can be shown[50] that for rotational motion in the extreme narrowing limit, $\omega_o \tau_c \ll 1$:

$$R_1^{ROT} = R_2^{ROT} = \frac{2\gamma^4 \hbar^2 I(I+1)}{r^6} \tau_c$$

The dependence of the dipole-dipole mechanism on the inverse sixth power of the separation of the nuclei, indicates that this mechanism is effective only over short ranges. If I and S are not contained on the same molecule then the dipole-dipole mechanism becomes intermolecular rather than intramolecular and in such situations τ_c is a translational correlation time rather than a rotational correlation time. However, due to the r^6 dependence the intermolecular mechanism is normally ineffective

in relaxing the I nucleus, (I not proton) thus, the intra-molecular mechanism is dominant, especially if S is directly bound to I.

B. Spin-rotation relaxation.

This relaxation mechanism results from the interaction of the nucleus I with magnetic fields generated by the motion of the molecular magnetic moment, arising from the electron distribution in the molecule. As the molecule rotates, a particular electron will rotate about the nucleus at a distance R, the rotational frequency, V, being given by

$$V = \frac{h\,J}{2\pi I}$$

where the molecule is in the Jth rotational state and I is its moment of inertia. The electron gives rise to a current, i

$$i = (e/c)V$$

The magnetic moment, μ_J, associated with this circulating current is given by

$$\mu_J = i(\pi R^2) = \frac{e\,h}{\pi M c}\,J \approx \mu_N J.$$

and $I = MR^2$, where M is the nuclear mass and μ_N is the nuclear magneton. This magnetic moment produces a local magnetic field at the nucleus which is modulated by collisions causing changes in both direction and rotation, thus, giving rise to a potential relaxation pathway.

Next to dipolar relaxation, spin-rotation is the most important relaxation mechanism for spin ½ nuclei. Since, it is proportional to the rotational velocity and inversely proportional to the moment of inertia, it would be expected that the smaller the molecule the more important the spin-rotation mechanism.

C) Chemical shift anisotropy (CSA)

Section 1.5.1.2. stated that the field at the nucleus is given by

$$B_{loc} = B_o (1-\sigma)$$

where σ is the screening factor. In fact, σ is direction dependent and should be represented by a tensor. In liquids only the average value or trace is observed.

$$\sigma = 1/3 (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

However, if the shielding is anisotropic, the nucleus experiences fluctuating fields as the molecule rotates, and, hence, may act as a relaxation mechanism.

CSA is frequently an inefficient relaxation mechanism but does depend upon B_o^2. Therefore, at high fields for nuclei with large shift anisotropies the mechanism can be the dominant one, (e.g. Hg^{51}, Tl^{52}).

D) Scalar relaxation

If a nucleus, I, is spin-spin coupled to a second nucleus, S, it is possible for S to provide a fluctuating magnetic field and, hence, a relaxation mechanism for I, by way of scalar interactions

involving the bonding electrons. The fluctuating magnetic field can arise from two sources. Firstly there may be a time dependence of the spin-coupling constant, resulting from, for example, chemical exchange, and secondly there may be a time dependence of the excited state of S. The first case leads to what is termed scalar coupling of the first kind and the latter to scalar coupling of the second kind. To be an efficient T_1 relaxation mechanism the fluctuations must be in the order of the Larmor freqeuncy. Therefore, exchange must be very rapid or the lifetime of the excited state of S very short for the mechanism to be efficient.

E) Quadrupolar relaxation.

Nuclei with spin $> \frac{1}{2}$ have an additional relaxation mechanism resulting from a fluctuating electric field. Nuclei with spin $\frac{1}{2}$ have a spherical nuclear charge distribution, however, nuclei with spin $> \frac{1}{2}$ have a non-spherical charge distribution resulting in their having a quadrupole moment. Such quadrupolar nuclei do not have an electric dipole moment, hence, their energy, is independent of orientation in a uniform electric field. Where an electric field gradient exists the nuclei precess about the net electric field, and in doing so provide a relaxation mechanism.

For nuclei of spin $> \frac{1}{2}$, quadrupolar relaxation dominates all other mechanisms, unless the electric field gradient is zero.

F) Electron-nuclear relaxation.

Since an electron has spin $\frac{1}{2}$ it, therefore, possesses a magnetic moment. Thus, an unpaired electron will generate fluctuating magnetic fields as the molecule moves in solution, and so can be a cause of relaxation. This mechanism is dipolar in nature and

so depends upon the size of the magnetic moment. For an electron, the magnetic moment is 10^3 times bigger than for a proton and, thus, electron-nuclear relaxation is 10^6 times more efficient than nuclear-nuclear relaxation. For this reason very small amounts of paramagnetic species in a sample can significantly affect relaxation times, and since dissolved oxygen is likely to be the most common paramagnetic species in a sample, it is necessary to degas samples before measuring relaxation times.

1.5.1.5. Measurement of spin-lattice relaxation times (T_1).

T_1 measurements are usually made by the 180^0-τ-90^0 pulse sequence, also termed inversion recovery. A 180^0 pulse inverts the magnetisation along the z' axis. Spin-lattice relaxation causes M_z, to recover to its equilibrium position M_o. If a 90^0 pulse is applied at some time, τ, after the 180^0 pulse the magnetisation will be rotated onto the y' axis and may be observed as an FID in the usual way. After a suitable delay of approximately $5T_1$, to allow the magnetisation to fully recover, the experiment is repeated using different values of τ. The recovery of the magnetisation is given by the expression

$$M_\tau = M_o \{1-2 \exp(-\tau/T_1)\}$$

For short values of τ the magnetisation is inverted and as τ is increased it becomes positive until it reaches M_o. T_1 can therefore be calculated from a plot - ln $(M_\infty - M_\tau)$ vs. τ.

1.5.1.6. The Nuclear Overhauser Effect (N.O.E.).

The N.O.E. is a change in the integrated N.M.R. signal of a spin when the N.M.R. absorption signal of another spin is saturated

by a strong second radiofrequency, as occurs in the process of spin decoupling. If I and S are two nuclei (S = proton) the nuclear Overhauser enhancement factor, η, is given by

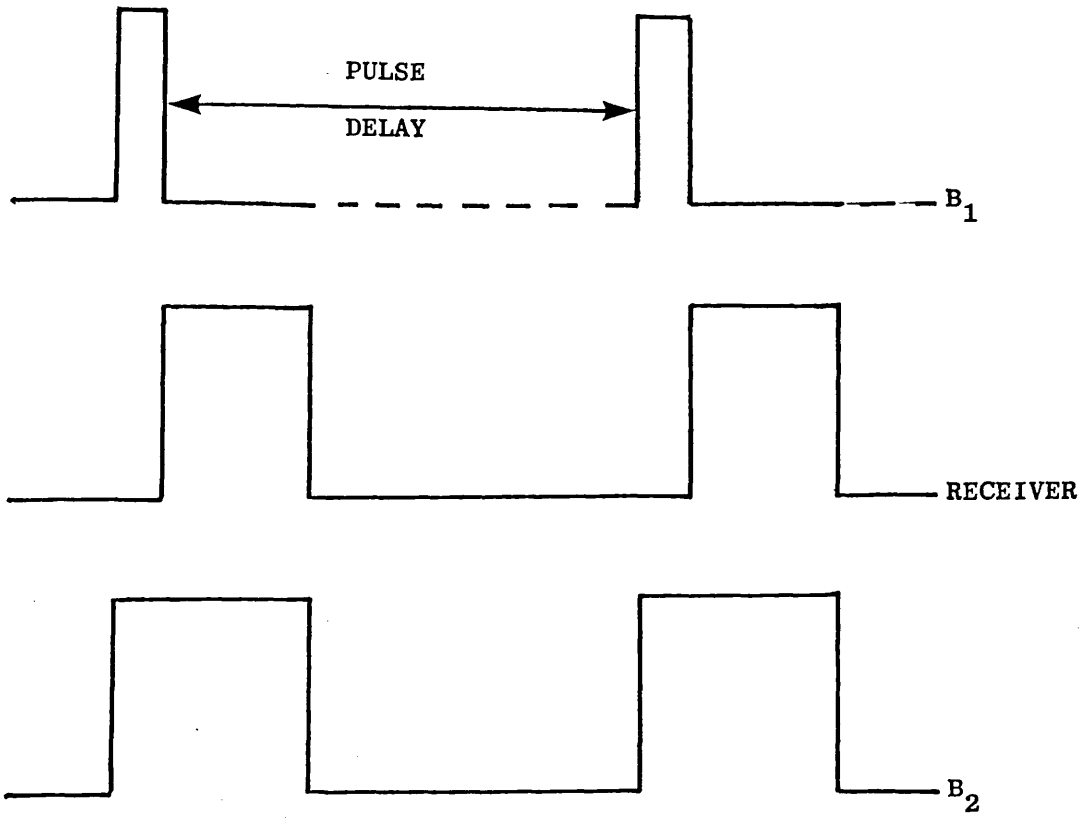
$$\eta = \frac{\gamma_S}{2\gamma_I}$$

and the maximum change in signal intensity on proton decoupling is given by

$$\text{N.O.E.} = 1 + \frac{\gamma_S}{2\gamma_I}$$

It is apparent that for a nucleus, I, having a negative magnetogyric ratio, γ_I, (cf. ^{29}Si, ^{119}Sn), the N.O.E. will be negative and hence a decreased signal intensity will result.

The N.O.E. arises from the dipole-dipole contribution to the spin-lattice relaxation. Therefore, a relaxation rate of which only half is due to the dipolar mechanism will show only half the maximum N.O.E.. In this way the N.O.E. may be used to determine the dipolar contribution to the overall relaxation rate. The change in intensity of a resonance due to the N.O.E. may be determined by comparing spectra obtained with and without the Overhauser enhancement. It is possible to obtain a spectrum without the N.O.E., since decoupling of S is virtually instantaneous, whereas, the I magnetisation resulting from this irradiation develops with a time constant of the spin-lattice relaxation time, T_1. Therefore, by use of gated decoupling, in which a timing sequence as shown below is employed, a spectrum without the N.O.E. is obtained.



To obtain a spectrum with a totally suppressed N.O.E. it has been found that the pulse delay time should be at least $8T_1$.[53] If the decoupling field, B_2, is left on throughout the experiment, a decoupled spectrum with N.O.E. is obtained.

If the intensity of the spectrum obtained using gated decoupling is denoted by I_G, and the intensity obtained using normal decoupling by I_N, the nuclear Overhauser factor, η, is given by

$$\eta = \frac{I_N}{I_G} - 1$$

If η_{MAX} is the maximum enhancement factor, the dipolar relaxation rate, R_1^{DD}, may be extracted from the total relaxation rate, R_1^{TOT}, from the expression

$$R_1^{DD} = \frac{\eta}{\eta_{MAX}} R_1^{TOT}$$

1.5.1.7. ^{119}Sn N.M.R. studies of organotin compounds.

Elemental tin has ten naturally occurring isotopes of which only three - ^{115}Sn, ^{117}Sn and ^{119}Sn - have non-zero nuclear magnetic moments. These isotopes each have a nuclear spin $I = \frac{1}{2}$ and approximately equal magnetic moments. However, because of its slightly better N.M.R. sensitivity and higher natural abundance, (Table IV), N.M.R. investigations of organotin compounds are usually carried out on ^{119}Sn.

Table IV[54]: Nuclear magnetic moments and natural abundance of the magnetic tin isotopes.

Isotope	Nuclear magnetic moment, μ (nuclear magnetons)	Natural abundance (%)	Relative N.M.R. sensitivity[a]
^{115}Sn	- 0.9132	0.35	3.5×10^{-2}
^{117}Sn	- 0.9949	7.67	4.5×10^{-2}
^{119}Sn	- 1.0409	8.68	5.2×10^{-2}

[a]At constant field ^{1}H = 1.00.

Due to the low N.M.R. sensitivity of ^{119}Sn compared to ^{1}H difficulties arise in obtaining spectra by direct observation using the C.W technique. However, the determination of ^{119}Sn chemical shifts was greatly facilitated by the use of an indirect method suggested by McFarlane and his coworkers[55], termed ^{1}H - (^{119}Sn) heteronuclear double magnetic resonance, (HDMR). In the ^{1}H spectrum of an organotin sample, satellites due to coupling of protons with ^{119}Sn and ^{117}Sn nuclei are in many cases observable. If the sample is simultaneously irradiated with a second R.F. at the resonance frequency of the ^{119}Sn nuclei, the satellites

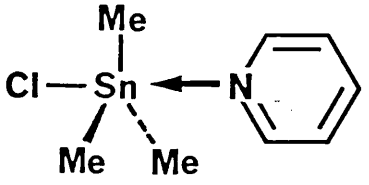
due to ^{119}Sn are decoupled and collapse into a single peak. Depending upon the amplitude of the second R.F. and accuracy of the R.F. setting, this irradiation can cause perturbations of the energy levels in the spin system. These perturbation patterns indicate the positions of the individual ^{119}Sn lines in the spectrum and so the ^{119}Sn chemical shift can be determined. The ^{1}H - (^{119}Sn) HDMR method has advantages over direct CW observation in that chemical shifts may be measured with greater accuracy and at lower concentration, since the ^{1}H spectrum gives much stronger signals than ^{119}Sn by direct observation. The disadvantage of the technique, however, is that chemical shifts can only be determined if the spin-spin coupling constants, $J(^{119}Sn-H)$, are significant in the proton spectrum.

An improvement in double resonance techniques may be achieved by the use of HDMR in the INDOR mode. In this method the detecting frequency is set exactly on the resonance of some ^{119}Sn satellite in the proton spectrum, while the perturbing frequency is swept over the resonance of the ^{119}Sn nuclei present in the sample. In this way, the spectra of ^{119}Sn multiplets, for example, may be recorded. This method is still, however, dependent upon the ^{119}Sn satellites being prominent in the proton spectrum. Obviously, in cases where the proton spectrum is very complex, or where a mixture of organotin compounds is present in the same sample, it is not easy to apply double resonance techniques. In these cases, or where lower concentrations are encountered, ^{119}Sn spectra are only successfully obtained by direct observation using pulse Fourier transform N.M.R. techniques.

The range of ^{119}Sn chemical shifts has been found to exceed 1800 p.p.m.[56], the shielding constant for ^{119}Sn being dominated by the paramagnetic term, σ_p, which is affected by many components, e.g. coordination number and bond hybridisation (Section 1.5.1.2).

Figure III shows the range of ^{119}Sn chemical shifts of some organotin compounds in non-coordinating solvents[57].

It has been observed by various workers[55,56,58] that five and six coordinate organotin compounds show ^{119}Sn signals which occur at much higher field than those of four coordinate compounds. Therefore, the choice of solvent when recording ^{119}Sn spectra is very important since a coordinating solvent, such as acetone, dimethyl sulphoxide (DMSO) or pyridine, will produce an increase in coordination number of the organotin compound and corresponding upfield shift. For example, the ^{119}Sn chemical shift of dimethyltin dichloride in DMSO (-246 p.p.m.) is almost 400 p.p.m. upfield from the value obtained in CCl_4[59]. The concentration of the sample is also important when polar solvents are used. For example, the addition of pyridine to a solution of trimethyltin chloride in carbon tetrachloride has been found[60] to produce a change in shift from +159 to -9 p.p.m. as the mole ratio of trimethyltin chloride to pyridine is altered from 1:0 to 1:12. This change of chemical shift is consistent with the formation of a five-coordinate trigonal bipyramidal adduct[1].

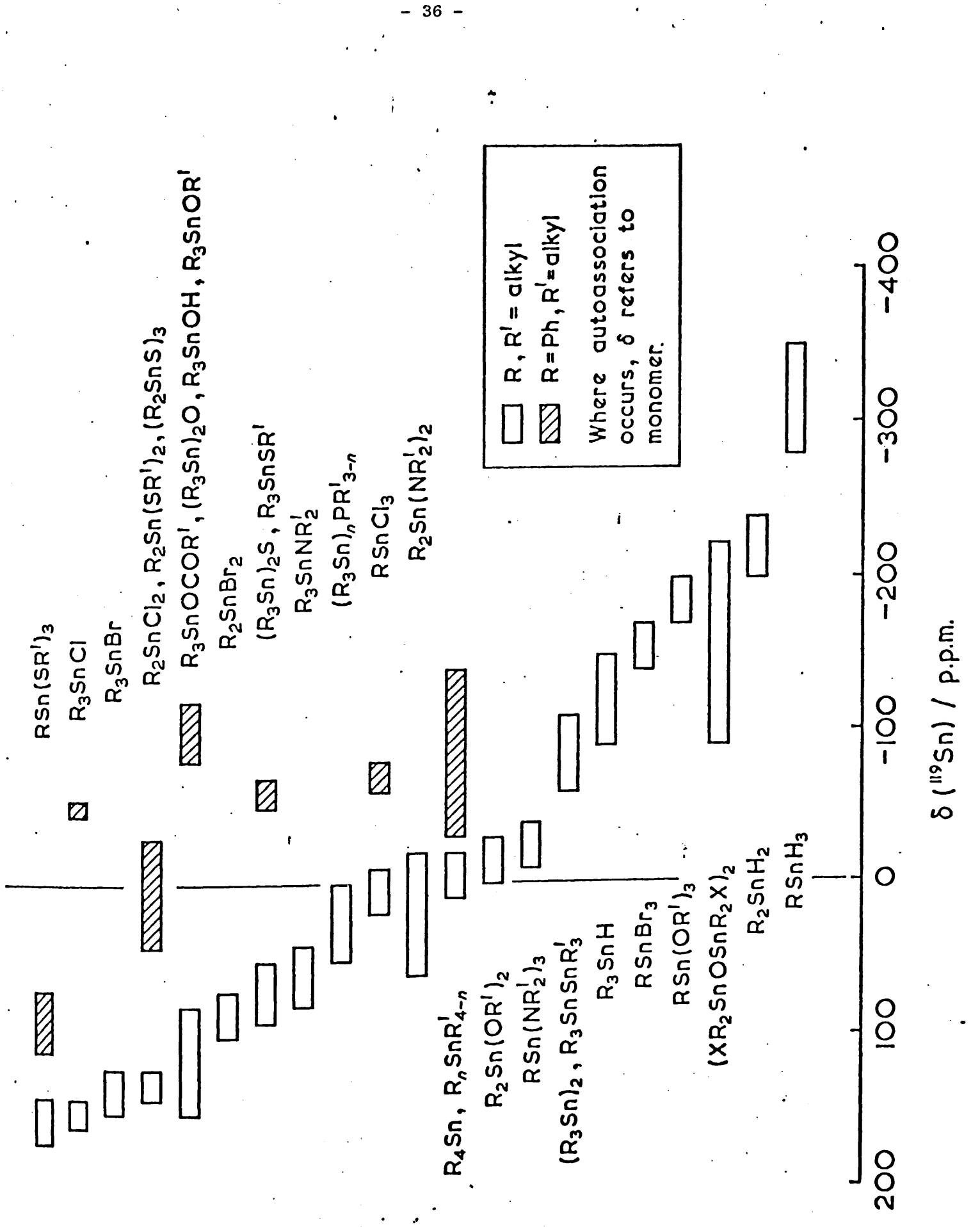


In non-coordinating solvents, such as carbon tetrachloride, the ^{119}Sn chemical shift has been found[58] to be virtually unaffected by concentration.

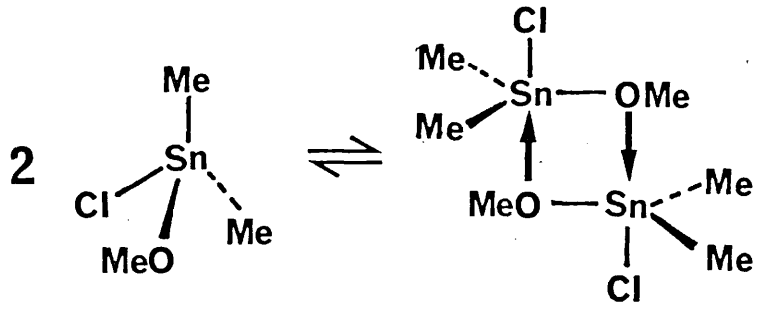
Auto-association of organotin compounds in solution causes large changes in chemical shift values, again due to changes in coordination

FIGURE III

^{119}Sn chemical shifts, $\delta(^{119}Sn)$ p.p.m., relative to Me_4Sn, of organotin compounds in non-coordinating solvents.[57]


RSn(SR')3
R3SnCl
R3SnBr
R2SnCl2, R2Sn(SR')2, (R2SnS)3
R3SnOCOR', (R3Sn)2O, R3SnOH, R3SnOR'
R2SnBr2
(R3Sn)2S, R3SnSR'
R3SnNR'2
(R3Sn)nPR'3-n
RSnCl3
R2Sn(NR'2)2
R4Sn, RnSnR'4-n
R2Sn(OR')2
RSn(NR'2)3
(R3Sn)2, R3SnSnR'3
R3SnH
RSnBr3
RSn(OR')3
(XR2SnOSnR2X)2
R2SnH2
RSnH3
R, R' = alkyl
R=Ph, R'=alkyl
Where autoassociation occurs, δ refers to monomer.
200
100
0
-100
-200
-300
-400
δ (119Sn) / p.p.m.

number. For example, dimethyltin methoxide chloride in dichloromethane shows[61] two resonances at +126 and -90 p.p.m. This is due to the equilibrium existing between the tetrahedral monomer and the dimer which contains five-coordinate tin.



^{119}Sn chemical shifts are also, as expected, affected by substituents. As the electron releasing power of the alkyl group increases, the tin atom becomes increasingly more shielded and so a move to higher field is obtained, while an increase in the electronegativity of an inorganic species attached to tin causes deshielding and a move to lower field.

The measurement of spin-spin coupling constants involving ^{119}Sn and a number of other nuclei has also received considerable attention and a selection of reported values are summarised in Table V[57].

The majority of literature involving ^{119}Sn N.M.R. is, therefore, concerned with chemical shifts and spin-spin coupling constants. Very little information is at present available concerning spin-lattice relaxation behaviour of the ^{119}Sn nucleus.

TABLE V[57]: Spin-spin coupling constants between ^{119}Sn and various nuclei in alkyltin compounds, R_nSnX_{4-n}, in non-coordinating solvents.

Compound	$^mJ(^{119}Sn-X)$ (Hz)	X	m	Ref.
Me_3SnH	1744	^1H	1	59
Me_4Sn	54	^1H	2	60
$MeSnCl_3$	100	^1H	2	59
Me_2SnCl_2	69	^1H	2	59
Me_3SnCl	58.5	^1H	2	61
$\{Me_3Sn(H_2O)_2\}^+Cl^-$	68.4	^1H	2	61
R_4Sn	300-340	^{13}C	1	62
R_4Sn	10-25	^{13}C	2	62
R_3SnX(4-coord)	330-390	^{13}C	1	62
R_3SnX(5-coord)	450-480	^{13}C	1	62
R_2SnX_2(4-coord)	370-480	^{13}C	1	62
R_2SnX_2(6-coord)	900-970	^{13}C	1	62
$(PhMe_2CCH_2)_3SnF$	2298	^{19}F	1	63
Me_3SnCF_2H	265.5	^{19}F	2	64
$(CF_3)_4Sn$	531	^{19}F	2	65
$Me_3SnCF_2CF_2H$	249.5	^{19}F	2	66
$Me_3SnCF_2CF_2H$	10	^{19}F	3	66
Me_3SnPPh_2	596	^{31}P	1	67
$(Me_3Sn)_2PPh$	724	^{31}P	1	67
$(Me_3Sn)_3P$	832.5	^{31}P	1	67
$Me_3SnB(NME_2)_2$	953	^{11}B	1	68
R_3SnSnR_3	700-4500	^{119}Sn	1	69
$R_3SnSnR_2SnR_3$	400-3000	^{119}Sn	1	69
$R_3SnSnR_2SnR_3$	200-800	^{119}Sn	2	69
$Me_3SnSiMe_3$	656	^{29}Si	1	68

Puskar et al[73] carried out the first spin-lattice relaxation study of an organo-tin compound in the liquid state. They measured the ^{119}Sn and ^{13}C spin-lattice relaxation times in the R_4Sn series (R = Me, Et and Pr) and in the trimethyltin halides, Me_3SnX (X = Br, Cl and I), over a range of temperatures. The T_1 values ranged from 0.5 - 5 secs. and the temperature dependence of the relaxation indicated that the spin-rotation mechanism was dominant over the whole temperature range only for Me_4Sn. For Et_4Sn and Pr_4Sn, spin-rotation dominated at higher temperatures, while, at lower temperatures dipole-dipole relaxation was the most important mechanism. In the Me_3SnX series, spin-rotation was the major relaxation mechanism; scalar relaxation contributed only when X = I.

Lassigne and Wells[74,75] studied Me_4Sn and its deuterated modifications, $(CH_3)_n\ Sn(CD_3)_{4-n}$, and found that the spin-rotation relaxation rate varied according to the square root of the moment of inertia. They also showed a correlation between the spin-rotation relaxation rate and the paramagnetic term of the shielding tensor of the ^{119}Sn nucleus.

Sharp[76] measured the spin-spin and spin-lattice relaxation times as a function of temperature for $SnCl_4$ and SnI_4, and Ahmed[77] used the differential relaxation rates of the central and satellite features in the ^1H spectrum of a number of organotin hydrides to derive the correlation times (τ_c) for the tin-hydride proton vector.

Mitchell[78], in a paper not directly concerned with relaxation, noted that significant N.O.E. factors were observed for hexabutylditin and hexaoctylditin, and Frangou[79] in a study of the spin-lattice relaxation, over a range of temperatures, of a number of organotin compounds, found the dipolar relaxation mechanism to be more important than previous results had indicated.

The simplicity of a proton-decoupled ^{119}Sn N.M.R. spectrum, together with the wide range of ^{119}Sn chemical shifts, makes the technique particularly useful for studying organotin compounds. Information is immediately obtained from the ^{119}Sn spectrum regarding the number of tin species present and their coordination number. Thus, in conjunction with ^{1}H and ^{13}C spectra, multinuclear N.M.R. spectroscopy is a particularly powerful analytical technique. The importance of the method in organotin chemistry is reflected in the number of review articles[49,54,62,80,81] dealing with N.M.R. studies of organotins which have appeared over the past few years.

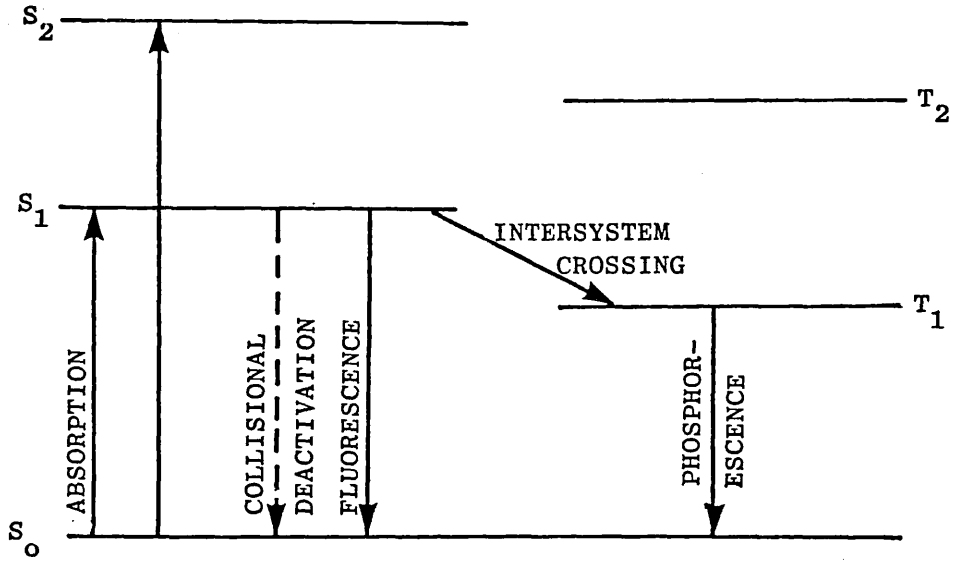
1.5.2. Spectrofluorescence

1.5.2.1. Theory

When light impinges upon matter, two things can occur. Either the light passes through the matter with no absorption taking place, or it may be absorbed. In the latter case, energy is transferred to the molecule in the absorption process.

Every molecule possesses a series of closely spaced energy levels and can undergo excitation from a lower to a higher energy state by the absorption of a discrete quantum of light equal to the difference between the two energy levels. Having absorbed energy and reached one of the higher vibrational levels of an excited singlet state, the molecule rapidly loses its excess vibrational energy by collision and falls to the lowest vibrational level of the excited state. From this level, the molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence. However, it is possible for the spin of the electron to be reversed, forming an excited triplet state. This can occur in many molecules when the energy of the lowest vibrational level

of the excited singlet state is equal to that of an upper vibrational level of the excited triplet state. The molecule can then return directly to the ground state from the excited triplet state, emitting energy in the form of phosphorescence. For fluorescence, the molecule can exsist in the excited state for only about 10^{-4} secs., whereas, for phosphorescence, transition times involved are 10^{-4} - 10^{2} secs. Hence, a characteristic feature of phosphorescence is that emission continues after the exciting source is removed. The energy changes involved in fluorescence and phosphorescence are illustrated below.



The fluorescence normally observed in solutions is the re-emission of less energetic photons than those absorbed and is called Stokes fluorescence. The decrease in energy is caused by the loss of some energy in the brief period before emission can occur, e.g. by molecular collision. If thermal energy is added to the excited state, or if a compound has many highly populated vibrational energy levels, emission at a higher energy than that of absorption can occur. This is known as anti-Stokes fluorescence and may be observed in dilute gases at high temperatures. The emission of photons possessing the same energy as the absorbed photons is known as resonance

fluorescence. This is never observed in solution, due to solvent interactions, but can occur in gases and crystals, and is the basis of atomic fluorescence.

If an electron is excited by an absorbed photon to a higher vibrational level without an electronic transition, energy is totally conserved and a photon of the same energy is emitted within 10^{-15} secs., as the electron returns to the ground state. This effect is known as Rayleigh scattering and is a problem when the intensity of fluorescence is low compared to the intensity of exciting radiation or when the absorption and emission spectra are close together. Another form of scattered emission is the Raman effect. Raman scatter appears at higher and lower frequencies than the Rayleigh scatter peak, with a constant frequency difference from the exciting radiation. Raman bands are much weaker than the Rayleigh scatter peak, but become significant if high intensity sources are used.

Any fluorescent compound has two characteristic spectra, the excitation spectrum and the emission spectrum. The shape of the excitation spectrum should be identical to the absorption spectrum of the compound. A general rule in choosing the excitation wavelength is that, if possible, the longest wavelength peak in the excitation spectrum is used. This minimises any possible photodecomposition by higher energy radiation.

1.5.2.2. Factors affecting fluorescence

A) Structural effects

Fluorescence phenomena are not usually sensitive to the finer details of molecular structure, and the method does not, therefore, have a wide application as a fingerprinting technique for unknown compounds. However, in order to understand the effects

that structure does have in fluorescence, it must be realised that fluorescence competes with other methods of energy loss, such as nonradiative decay or photochemical reaction. Generally, for a molecule to fluoresce, it should possess the following characteristics:-

1) The spin-allowed electronic absorption transition of lowest energy should be very intense. Since fluorescence is the reverse of absorption, it follows that, the more probable the absorption transition, the more probable will be the fluorescence transition.

2) The energy of the spin-allowed absorption transition should be reasonably low. Obviously, the higher the energy of excitation, the more probable the occurrence of photodissociation.

3) The electron that is promoted to a higher energy level should not be strongly involved in bonding, otherwise bond dissociation may occur, with electronic excitation, and fluorescence is unlikely to be observed.

4) The molecule should not contain structural features or functional groups that enhance radiationless transitions.

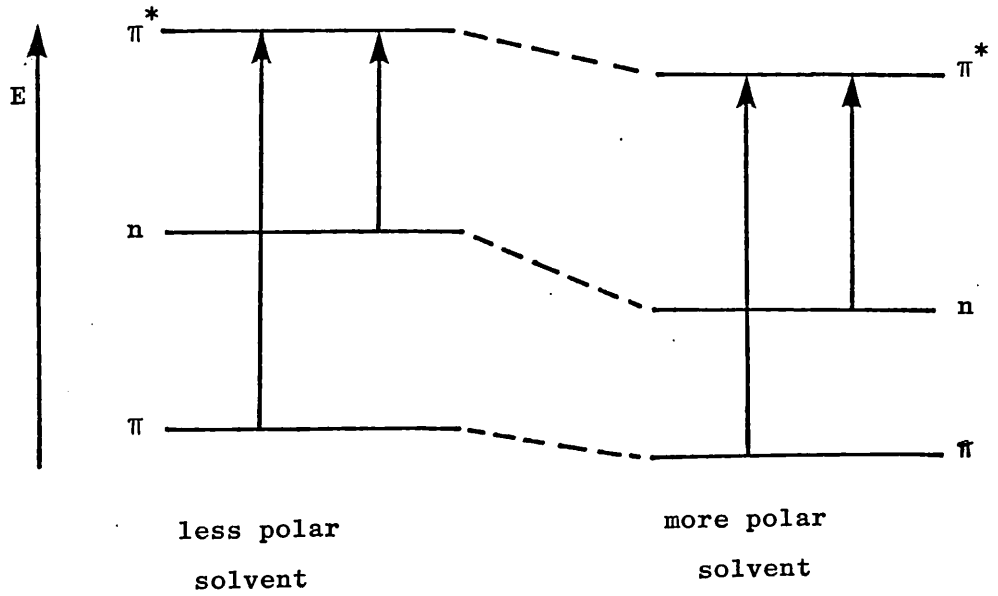
If these conditions are considered, it may be understood why aromatic compounds tend to be highly fluorescent. In aromatic molecules, π-electrons, which are less strongly held than σ-electrons, can be promoted to π^*- antibonding orbitals by the absorption of fairly low energy radiation, without severely disrupting bonding. Also these $\pi \rightarrow \pi^*$ transitions are strongly allowed, thus, compounds containing low-lying (π, π^*) singlet states, are usually highly fluorescing.

In saturated hydrocarbons, transitions involving σ-electrons occur at very high energies and significantly disrupt bonding.

It would, therefore, be expected that such compounds either do not fluoresce at all, or, if they do fluoresce, the intensity of the emitted radiation will be very small.

B) Solvent-effects.

The position of both the absorption and emission spectra may be altered when recorded in different solvents. This is due to the way in which polar solvents stabilise different orbitals. For example, $\alpha\beta$ unsaturated ketones show two absorptions due to the transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Polar solvents stabilise all three orbitals, but not all to the same degree. The stabilisation of the nonbonding orbital is particularly pronounced with hydrogen-bonding solvents and π^* orbitals are more stabilised than π, presumably because π^* is more polar. Consequently, the net result is that the $\pi \rightarrow \pi^*$ transition moves to lower energy, while $n \rightarrow \pi^*$ moves to higher energy.



Although the direction of the shift in the absorption and emission spectra is general, the magnitude is usually related to the dielectric constant of the solvent.

C) Effect of pH.

Relatively small changes in pH can sometimes radically affect the intensity and spectral characteristics of fluorescence. This effect can, however, be put to an advantageous use in that it may be used as a parameter in fluorimetric analysis to reduce interference by extraneous solutes in a mixture, or to obtain the most strongly fluorescent species for analysis.

D) Effect of hydrogen bonding.

Fluorescence behaviour can be greatly affected by hydrogen bonding interactions with the solvent or other solutes present.

If it is assumed that a solute molecule, A, can hydrogen bond with another molecule or the solvent, B, formation of a hydrogen-bonded complex between the two may exist in the excited state, formed by excitation of the species present in the ground state.

$$A - B \xrightarrow{h\nu} (A - B)^*$$

Alternatively, hydrogen bonding with B may occur with an already excited A^*.

$$A \xrightarrow{h\nu} A^*, \quad A^* + B \longrightarrow (A - B)^*$$

In the former case, both the absorption and emission spectra will be affected by hydrogen bonding with B, whereas, in the latter case, only the emission spectrum is affected.

It is often found that excited state hydrogen-bonding reduces the quantum yield of fluorescence, ØF, of A, where

$$\text{Quantum yield, } \emptyset F = \frac{\text{No. of quanta emitted}}{\text{No. of quanta absorbed.}}$$

Thus, as a general rule, when performing a quantitative fluorescent determination of molecules containing such groups as -OH, $-CO_2H$, $-NR_2$ or -SH, a solvent should be chosen which will not hydrogen bond strongly with the molecule.

E) Effects of other solutes.

The fluorescent properties of a compound may be affected not only by the solvent but also by interaction with other solutes present in solution. There are many solute-solute interactions and many of them cause fluorescence quenching.

Fluorescence quenching by electronic energy transfer.

If a solute, A, is present in a sample containing one or more other solutes, Q, which have excited singlet states lower in energy than the first excited singlet of A, electronic energy transfer to that solute may occur:

$$^1A^* + Q \longrightarrow A + {}^1Q^*$$

A number of mechanisms for this singlet-singlet energy transfer may be considered:

a) Absorption of $^1A^*$ fluorescence by Q.

This process may be represented as follows:-

$$^1A^* \longrightarrow A + h\nu \; : \; h\nu + Q \longrightarrow {}^1Q^*.$$

It is significant only if the absorption spectrum of Q overlaps the emission spectrum of A, and if the concentration of Q is sufficiently large for its absorbance to be at least 0.05 in the region of overlap. If A and Q are present in the sample in approximately equal amounts, the quenching by Q can be suppressed simply by diluting the solution, so that the absorbance of Q is very low. However, if A is only a minor constituent relative to Q, the components must be separated.

b) Collisional non-radiative transfer.

Non-radiative energy transfer from $^1A^*$ to Q occasionally requires collisional interaction. Such processes occur at or near the diffusion controlled rate, which depends upon the viscosity of the medium.

Collisional quenching usually obeys the Stern-Volmer equation:

$$\frac{\phi F}{\phi F^0} - 1 = K_Q \quad \tau_{F^0} \quad \{Q\}$$

ϕF = quantum yield in the presence of Q

ϕF^0 = quantum yield in the absence of Q

$\{Q\}$ = concentration of Q

K_Q = bimolecular quenching rate constant

τ_{F^0} = excited state lifetime of $^1A^*$ in the absence of Q.

Diffusion controlled quenching can be lessened by increasing the viscosity of the solvent or by decreasing the concentration of Q by dilution, but again dilution will not overcome the problem if A is only a relatively small component compared to Q.

Fluorescence quenching by oxygen.

Perhaps the most common and abundant fluorescence quencher is molecular oxygen and some compounds are far more susceptible to this form of quenching than others. It seems that the most likely mechanism of oxygen quenching is by enhanced singlet-triplet intersystem crossing. This does not mean, however, that the sensitivity of phosphorescence is necessarily increased, since the lifetime of the triplet state is much longer than the lifetime of the singlet state and the possibility of collisional quenching therefore becomes greater.

F) Effect of solute concentration.

It is usually found that fluorescence intensity increases linearly as a function of concentration. However, this is only true at relatively low concentrations, and, at higher concentrations, it may be found that the fluorescence intensity reaches a maximum or, in some cases even decreases. At low concentrations, a fairly even distribution of absorption of the exciting light occurs along the light path. However, as the concentration becomes high, this even distribution no longer exists, since the portion of the solution nearest to the light source absorbs so much radiation that less and less is available for excitation of the rest of the solution. Thus, it may be seen how a maximum emission intensity may be reached. Other fluorescent effects related to concentration, which sometimes need to be considered are:-

a) Re-absorption of emitted radiation by a ground-state molecule can increase as concentration increases.

b) The possibility of forming dimers increases with concentration.

c) The possibility of forming excimers with ground state molecules also increases with concentration.

$$^1A^* + A \longrightarrow {}^1(A^* - A)$$

The excimer has its own characteristic emission spectrum shifted to lower energy than that of the monomer.

G) Effect of temperature.

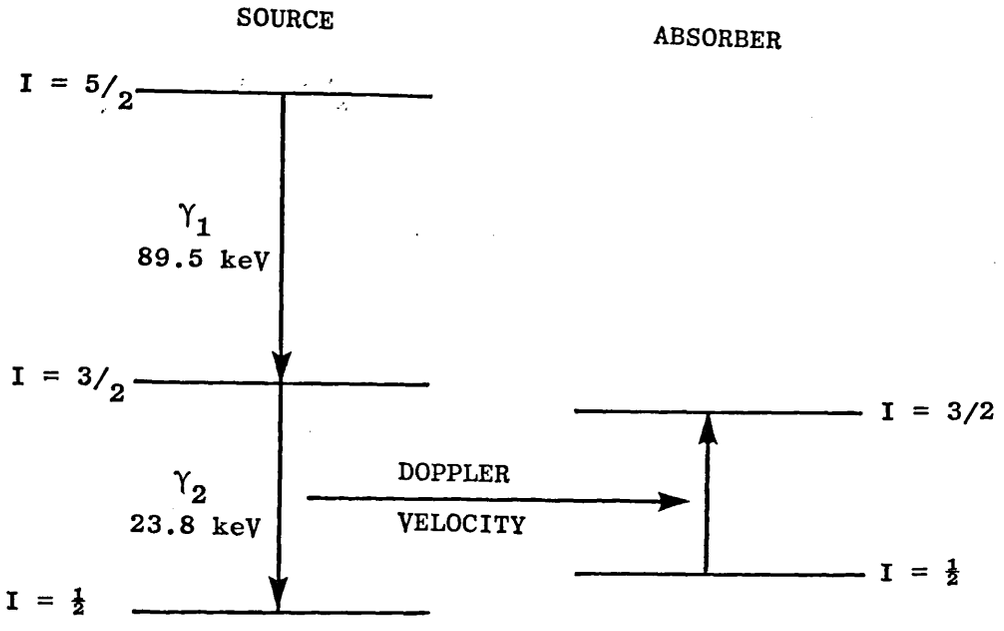
The main effect of temperature is to increase energy loss by molecular collision and, thus, reduce the fluorescence intensity. This effect changes from compound to compound, but, as a very general approximation, the change in fluorescence is approximately 1% per ^0C. However, in some compounds, this effect may be as high as 5%.

Further details of the factors affecting fluorescence measurements and experimental technique may be found in one of many standard texts.[82]

1.5.3. Mössbauer spectroscopy.

The use of Mössbauer spectroscopy in organotin chemistry provides valuable information regarding structure and coordination number of the tin atom. The radioactive tin source is typically Ca $^{119m}SnO_3$, the ^{119m}Sn isotope having a half-life of 245 days and decaying with the emission of two low-energy γ-rays (89.5 keV

and 23.8 keV), as illustrated below:



The principle of Mössbauer spectroscopy with regard to tin is that the ^{119}Sn isotope in the sample absorbs the 23.8 γ-ray emitted from the source and is consequently raised from the ground state ($I = \frac{1}{2}$) to the first excited state ($I = 3/2$). The exact energy required to accomplish this is, however, dependent upon the s electron density surrounding the ^{119}Sn nucleus. Therefore, the energy of the recoil-less 23.8 keV γ-ray is modified, by use of the Doppler effect, to correspond precisely to that required by the sample. The Doppler shift is achieved by imparting a relative motion between the source and the absorber.

The Mössbauer spectrum is characterised by two parameters - the isomer shift (δ) and the quadrupole splitting (ΔE_Q). The isomer shift reflects the difference in transition energy, $I = \frac{1}{2} \rightarrow I = 3/2$, between the source and the absorber, and is measured as the

velocity applied, in mm.sec.$^{-1}$, to achieve resonant absorption of the γ-ray.

If a nucleus has a spin-state greater than $\frac{1}{2}$, it will have a quadrupole moment, reflecting its non-spherical charge distribution,which interacts with electric field gradients arising from non-spherical electron distribution. The quadrupole moment can align itself either with or against the resulting field gradient at the nucleus, and the I = 3/2 excited state of ^{119}Sn will be split into a doublet, while the I = $\frac{1}{2}$ ground state, with zero quadrupole moment, will remain unaffected. The absorber will consequently display a two-line Mössbauer spectrum, with a separation between the peaks corresponding to the quadrupole splitting value, ΔE_Q, in mm.sec.$^{-1}$.

By comparison of these two parameters (δ and ΔE_Q) with previous results[83,84] information concerning coordination number and structure of the compound may be obtained. However, Mössbauer spectroscopy is limited in that it can only be applied to solids (usually at 80K) and since the peaks obtained are rather broad compared to the isomer shift, the technique cannot easily be applied to mixtures, where one species is in considerably greater amount than the others.

1.5.4. Infrared spectroscopy.

Molecular vibrations (bending and stretching of bonds) occur with frequencies corresponding to the infrared region of the electromagnetic spectrum. When a molecule is subjected to infrared radiation of a frequency corresponding to one of its natural vibration frequencies the radiation is absorbed and the particular vibration excited. Thus, by observing the infrared absorption frequencies of a compound it is possible to derive information about the types of bond in the molecule, and hence its functional groups.

Infrared spectra are normally recorded in the 'near infrared' or 'sodium chloride' region (600-4000 cm^{-1}) and information regarding organic functional groups may be obtained in this region. However, with the exception of ν(Sn-H) almost all fundamental stretching frequencies involving tin atoms occur in the "far-infrared" region (200-600 cm^{-1}) e.g. ν(Sn-C) and ν(Sn-Hal.).

Infrared spectroscopy does not lend itself to the analysis of a mixture of related compounds due to the complexity of the spectra and the fact that absorption frequencies are not greatly affected by the rest of the molecule, as are for example ^{119}Sn nuclear magnetic resonances.

1.6 Methods available for determining tin compounds at the µg and sub-µg level.

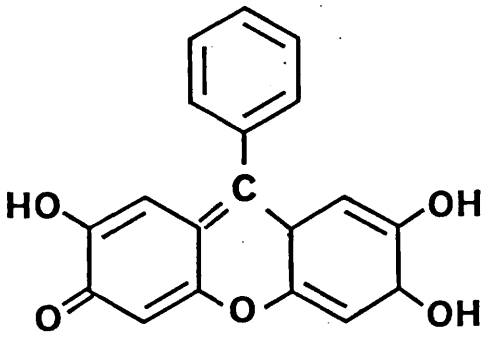
As world governments and authorities become increasingly, and rightly concerned with environmental pollution, it is becoming more important for methods of chemical detection and quantitative determination at trace levels to be developed.

The previous section discussed some of the physical methods which may be used for analysis of organotins. Although all of the methods provide, in one form or another, useful information and may, perhaps with the exception of fluorescence spectroscopy, be used as a 'finger-printing' technique for unknown compounds, neither N.M.R., I.R. nor Mössbauer spectroscopy possesses sufficient sensitivity to permit detection of specific compounds at very low levels. However, many different methods have been developed for the trace determination of tin and organotins.

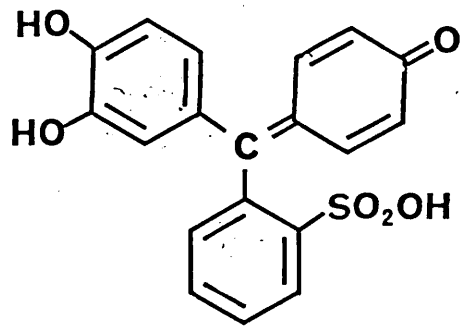
Flame atomic absorption spectroscopy, utilising an air - C_2H_2 flame can determine tin at levels of 1-2 p.p.m.[85]. It has been

reported[86] that the sensitivity obtained fron an air-H_2 flame is double that of the air-C_2H_2 flame, but the method is prone to interference. A C_2H_2-N_2O flame is claimed[87] to have a sensitivity somewhere between that of air-C_2H_2 and air-H_2, but without the interference of the latter. Atomic fluorescence has also been used for the determination of tin. This utilises a nitrogen separated argon-oxygen-hydrogen flame and is claimed to have a detection limit of 0.4 p.p.m.[88]. The sensitivity of atomic absorption has been increased by the recent introduction of electrothermal atomisation. Increases in sensitivity of up to 1000 times may be obtained over flame techniques. The main reason for this being that the excited atoms are contained within a graphite furnace and so are held in the light path for a longer period of time than in flame methods.

The determination of tin by visible absorption spectrophotometry has been widely investigated and at least 50 different photometric reagents have so far been reported[89]. Perhaps the most widely applied reagents are phenylfluorone (1), catechol violet (2) and 3-nitro-4-hydroxy-phenylarsonic acid (3).



(1)



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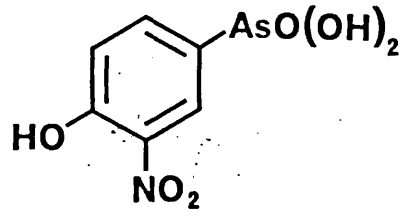


(3)

The first two reagents have approximately the same sensitivity, i.e. the smallest amount of tin that can be determined is ~ 2 μg[90,91]. The sensitivity of the catechol violet method can be increased to ~ 0.25 μg by removal of the excess reagent and measurement of the optical density in microcells[92]. 3-nitro-4-hydroxy-phenylarsonic acid[93] is a less sensitive reagent, about 50 μg being the smallest amount of tin that can be determined, but is more specific, with only Ti, W or Zr causing interference.

Spectrofluorescence has been used for the determination of tin and some organotins at the μg level, and these methods are reviewed in Section 3.2.

Alternative methods based on electroanalytical techniques have been applied to the determination of inorganic tin and some specific organotin compounds. Bond[94] investigated polarographic and anodic stripping voltametric techniques for the determination of tin and found alternating current anodic stripping voltametry to be the most sensitive, being able to determine .1 - .001 p.p.m. of tin. Fleet et al[95] studied the electrochemical behaviour of organotin compounds and found that with differential pulse polarography between .1 - .0005 p.p.m. of compound could be detected and Woggon et al[96] used anodic stripping voltametry for the determination of some organotin compounds and found that the detection limit was of the order of .05 p.p.m. for the compounds studied.

Neutron activation analysis, whilst generally not as sensitive for tin as the previously mentioned techniques has been shown to have a detection limit of 0.02 μg for inorganic tin[97].

Many of these analytical techniques cannot be used for the determination of specific organotins, since the final analysis

is made upon inorganic tin, or for instance with a non-specific photometric reagent. Therefore, in order that a particular organotin may be determined in a mixture, the analytical method must first incorporate a separation procedure i.e. a chromatographic technique. Examples of which are the use of gas-chromatography and mass spectrometry for the determination of butyltins in aqueous systems[99] and a gas-liquid chromatograph interfaced to an atomic-absorption spectrophotometer for the determination of organometallic gases[100].

1.7. References

1) R. Hulme, J. Chem. Soc., 1963, 1524.

2) E.O. Schlemper, Inorg. Chem., 1967, 6, 2012.

3) E.A. Blom, B.R. Penfold and W.T. Robinson, J. Chem. Soc., 1969, A, 913.

4) G.S. Brownlee, A. Walker, S.C. Nyburg and J.J. Szymański, Chem. Comm., 1971, 1073.

5) J.S. Morris and E.O. Schlemper, J. Cryst. Mol. Struct., 1978, 8, 295.

6) C.D. Garner, P. Sutton and S.C. Wallwork, J. Chem. Soc., 1967, A, 1949.

7) W.E. Bernett, D.E. Broberg and N.C. Baenziger, Inorg. Chem., 1973, 12, 930.

8) G.A. Ozin and A.van der Voet, J. Chem. Phys., 1972, 56, 4768.

9) F.R. Poulsen and S.E. Rasmussen, Acta Chim.Scand., 1970, 24, 150.

10) R. Rundle and D. Olsen, Inorg. Chem., 1964, 3, 596.

11) W.J. Moore and L. Pauling, J. Amer. Chem. Soc., 1941, 63, 1392.

12) R.D. Cremer, R.V. Lindsey,Jr., C.T. Prewitt and U.G. Stolberg, J. Amer. Chem. Soc., 1965, 87, 658.

13) W.P. Neumann, 'The Organic Chemistry of Tin', Wiley, New York, 1970.

14) H.A. Skinner, Advances in Organometallic Chemistry, 1964, 2, 49.

15) G.A. Nash, H.A. Skinner and W.F. Stack, Trans. Faraday Soc., 1965, 61, 640.

16) D. Meynier, Ph.D. Thesis, Univ. of Toulouse, 1955.

17) J.M. Barnes and L. Magos, Organomet. Chem. Rev., 1968, 3, 137.

18) P.J. Smith, I.T.R.I. Public. No.538.

19) C.J. Evans, Tin and its Uses, 1971, 87, 13.

20) L.B. Weisfeld and R.C. Witman, Ger. Pat. 2, 238, 148, 1973.

21) P.J. Smith and L. Smith, Chem. Brit., 1975, 11, 208.

22) S. Karpel, I.T.R.I. Publication No. 593.

23) G.J.M. van der Kerk and J.G.A. Luijten, J. Appl. Chem., 1954, 4, 314.

24) B.A. Richardson, Stone Ind., 1973, 8, 2; B.A. Richardson and T.G.R. Cox, Tin and its Uses, 1974, 102, 6.

25) Int. Tin Res. Coun. a Rep., 1973, p.480. Town: ITRI, 1974.

26) C.J. Evans and P.J. Smith, J. Oil Colour Chem. Ass. 1975, 58, 160; A.T. Philip, Progr. Org. Coatings, 1973/4, 2, 159.

27) N.F. Cardarelli, Tin and its Uses, 1972, 93, 16.

28) P. Dunn and D. Oldfield, Rubber Ind., 1975, 9, No.1.

29) 'Tin Chemicals for Industry', I.T.R.I. Publication, No.447, 1976.

30) C.J. Evans, Tin and its Uses, 1970, 86, 7.

31) E.H. Blair, Environ. Qual. Safety Suppl. 1975, 3, 406.

32) A.G. Bayer, U.S. Pat. 3, 907, 818, 1975.

33) Shell Oil Co., Brit. Pat.1, 327, 336, 1973.

34) J. Deufel, Fischwert, 1970, 20, 189.

35) R.W. Drisko, L.K. Schwarb and T.B. O'Neill, Proc. Contr. Rel. Plastic. Symp., Oregon State Univ., 1977, 181.

36) Y.M. Busygina, T.B. Zavarova, L.I. Pilyasova, Y.V. Ovchinnikov and B.F. Teplov, Plast.- Massey, 1971, 1, 55.

37) J.G. Pollard, J. Am. Coll. Health Assoc., 1967, 15, 234.

38) R.G. Tigner and J.F. Besser, Agric. and Food Chem., 1962, 10, 484.

39) T. Suzukawa, Seramikkusu, 1969, 4, 852.
Chem. Abs., 1970, 72, 58548.

40) B.J. Baliga and S.K. Ghandi, J. Electrochem. Soc., 1976, 123, 941.

41) J. Kane, H.P. Schweizer and W. Kern, J. Electrochem Soc., 1976, 123, 270.

42) M and T. Corp., Brit. Pat. 772, 646, 1957.

43) W.R. Jones NASA Tech. Note., TN. D-7175, 1975.

44) C.J. Faulkner. Neth. Pat. 227, 866, 1962.

45) W. Blochl, Fr. Pat. 1, 456, 631, 1965
F.M.C. Corp., U.S. Pat. 3, 423, 443, 1964.

46) Unitika Ltd., Ger Offen. 1, 958, 639, 1970.

47) R.R. Ernst and W.A. Anderson, Rev. Sci. Instrum., 1966, 27, 93.

48) C.J. Jameson and H.S. Gutowsky, J. Chem. Phys., 1964, 40, 1714.

49) J.D. Kennedy and W. McFarlane, Revs. Si, Ge, Sn and Pb Comps., 1974, 1, 235.

50) T.C. Farrar and E.D. Becker, 'Pulse and Fourier Transform NMR', Academic Press, 1971.

51) D.G. Gillies, L.P. Blaauw, G.R. Hays, R. Huis and A.D.H. Clague, J. Mag. Res., 1981, 42,

52) F. Brady, R.W. Matthews, M.J. Forster and D.G. Gillies, Inorg. and Nucl. Chem. Lett., 1981, In press.

53) S.J. Opella, D.G. Nelson and O. Jardetzsky, J. Chem. Phys., 1976, 64, 2533.

54) P.J. Smith and A.P. Tupciauskas, Ann. Reps. of N.M.R. Spectrosc., 1978, 8, 291.

55) A.G. Davies, P.G. Harrison, J.D. Kennedy, T.N. Mitchell, R.J. Puddephatt and W. McFarlane J. Chem. Soc. (C) 1969, 1136.

56) J.J. Burke and P.C. Lauterbur, J. Am. Chem. Soc., 1961, 83, 326.

57) A.G. Davies and P.J. Smith, in: "Comprehensive Organometallic Chemistry", ed. G. Wilkinson, Pergamon Press, London, 1981/82.

58) B.K. Hunter and L.W. Reeves, Can. J. Chem., 1968, 46, 1399.

59) J.D. Kennedy and W. McFarlane, J.C.S. Perkin II, 1974, 146.

60) L. Smith, Ph.D. Thesis, Univ. of London, 1972.

61) A.C. Chapman, A.G. Davies, P.G. Harrison and W. McFarlane, J. Chem. Soc. (C), 1970, 821.

62) V.S. Petrosyan, Progr. N.M.R. Spectrosc., 1977, 11, 115.

63) H. Druskamp and G. Stigmuir, Z. Naturforsch., 1967, 22a, 1458.

64) J.R. Holmes and H.D. Kaesz. J. Am. Chem. Soc., 1961, 83, 3903.

65) T.N. Mitchell, J. Organomet. Chem., 1973, 59, 189.

66) W. McFarlane and R.J. Wood Chem. Comm., 1969, 262.

67) W.R. Cullen, J.R. Sams and M.C. Waldman, Inorg. Chem., 1969, 262.

68) R.A. Jacob and R.L. Lagow, Chem. Comm., 1973, 105.

69) H.C. Clark, N. Cyr and J.H. Tsai, Can. J. Chem., 1967, 45, 1073.

70) W. McFarlane and D.S. Rycroft, J. Chem. Soc. Dalton Trans., 1974, 1977.

71) J.D. Kennedy, W. McFarlane, G.S. Pyne and B. Wrackmeyer, J. Chem. Soc. Dalton Trans., 1975, 386.

72) T.N. Mitchell and G. Walter, J. Chem. Soc. Perkin II, 1977, 1842.

73) Y.C. Puskar, T.A. Saluvere, E.T. Lippmaa, A.B. Pernin and V.S. Petrosyan, Doklady Akad. Nauk. SSSR, 1975, 220, 112.

74) C.R.E. Lassigne, Ph.D. Thesis, Simon Fraser Univ., 1975.

75) C.R.E. Lassigne and E.J. Wells, J. Mag. Resonance, 1977, 26, 55.

76) R.R. Sharp, J. Chem. Phys., 1972, 57, 5321.

77) M.J. Ahmed, Ph.D. Thesis, Univ. of London, 1977.

78) T.N. Mitchell, J.C.S. Perkin II 1977, 1842.

79) A. Frangou, Ph.D. Thesis, Univ. of London, 1979.

80) P.J. Smith and L. Smith, Inorg. Chim. Acta. Revs., 1973, 7, 11.

81) R.K. Harris, J.D. Kennedy and W. McFarlane, in "N.M.R. and the Periodic Table", ed. R.K. Harris and B.E. Mann, Academic Press, London, 1978, 342.

82) G.R. Guilbault, "Practical Fluorescence; Theory, Methods and Techniques". Marcel Dekker Inc., New York, 1973.

83) P.J. Smith, Organomet. Chem. Revs. A., 1970, 5, (3), 373.

84) J.N.R. Ruddick, Revs. Si, Ge, Sn and Pb Comps., 1976, 2, 115.

85) A.H. Chapman, Personal Communication.

86) L. Capacho-Delgado and D.C. Manning, Spectrochim. Acta, 1966, 22, 1505.

87) M.D. Amos and J.B. Willis, Spectrochim. Acta, 1966, 22, 1325.

88) R.F. Browner, R.M. Dagnall and T.S. West, Anal. Chim. Acta, 1969, 46, 207.

89) J.W. Price and R. Smith, Handbuch der Analytischen Chemie, Part III, Tin, Springer-Verlag, Berlin, 1978.

90) C.L. Luke, Anal. Chem., 1959, 31, (11), 1803.

91) E.J. Newman and P.D. Jones, Analyst, 1966, 91, 406.

92) L.H. Adcock and W.G. Hope, Analyst, 1970, 95, 868.

93) M. Jean, Anal. Chim. Acta, 1953, 8, (5), 432.

94) A.M. Bond, Anal Chem., 1950, 42, 1165.

95) B. Fleet and N.B. Fouzder, J. Electroanal. Chem., 1975, 63, 59.

96) H. Woggon, H. Sauerlich and W.J. Uhde, Z. Anal. Chem., 1972, 260, 268.

97) H.J. Bowen, Analyst, 1972, 97, 1003.

98) J. Herok and H. Gotte, Intern. J. Appl. Radiat. Isot., 1963, 14, (9), 461.

99) H.A. Meinema, T. Burger-Weersma, G. Verslius-de Haan and E. Ch.Gevers, Enviro. Sci. and Techn., 1978, 12, 288.

100) G.E. Parris, W.R. Blair and F.E. Brinckman, Anal. Chem., 1977, 49, 378.

CHAPTER 2

DEGRADATION OF ORGANOTIN COMPOUNDS

2.1. Introduction

Degradation of an organotin compound may be defined as the progressive removal of organic groups attached to the tin atom.

<u>i.e.</u> $R_4Sn \longrightarrow R_3SnX \longrightarrow R_2SnX_2 \longrightarrow RSnX_3 \longrightarrow SnX_4$

The question of degradation of organotins is one which needs to be considered in some detail due to the wide range of industrial applications of these compounds. In some cases, degradation of the organotin may be considered a problem, whereas in others it is perhaps a necessity. For example, in applications such as wood preservation, or P.V.C. stabilisation, the organotin is required to exist in its original form over a long period of time. Degradation in these situations could lead to a reduction in the effectiveness and active lifetime of the compound to perform its intended function. Thus, in these cases, it is stability that is required not degradation. On the other hand, in applications where there exists a risk of environmental pollution, for example as fungicides, pesticides and in antifouling paints the eventual degradation of the compound is a required event. The organotins which

show the highest biological activity are of the type R_3SnX (see Section 1.3.) and, consequently, it is these compounds that have attained biocidal uses. Obviously, it is not satisfactory for toxic materials to accumulate in the environment, and perhaps in the perfect situation a compound would be applied, perform its intended function and then immediately break down, leaving a totally non-toxic residue. Organotins might not be quite as perfect as this but, nevertheless, degradation of an R_3SnX compound produces progressively less toxic species (Section 1.3.) until, finally, only the non-toxic inorganic tin residue remains. It is through this process of degradation that organotins have an advantage over other organometallics, such as organomercury or organolead compounds where the breakdown products still retain a high degree of toxicity. Therefore, in order that an organotin compound may gain acceptance for environmental usage, it must be demonstrated that degradation does occur.

Further importance for studying the degradation of organotins, particularly of the methyltins, has arisen from the concern that has been shown over the possibility of the environmental methylation of inorganic tin. The environmental conversion of inorganic mercury(II) compounds to monomethyl- and dimethylmercury species became apparent in the 1960's, following the discovery that a large fraction of the mercury in fish was methylmercury(II) even though some of the fish were taken from lakes into which no methylmercury(II) compounds had been discharged. Two independent analytical investigations have recently been carried out, in the U.S.A., for trace amounts of organotins in the environment. Hodge *et al.*[1] claim to have found mono- and di-methyltin compounds in environmental water samples at concentrations of a few ng. per litre while Bramen and Tompkins[2] determined approximately the same level of mono-, di- and tri-methyltin species in various

natural water supplies and human urine. The implication of this wide distribution of methyltins is that environmental methylation of inorganic tin is possibly taking place. But, when particular uses of di- and mono-methyltins, for instance as stabilisers for P.V.C. potable water pipes in the U.S.A., are considered, the analytical findings cannot be taken as a definite proof of methylation. Wood et al.[3-5] found that, in the laboratory, certain tin(II) salts (e.g. $SnCl_3^-$) may be methylated by methylcobalamin (the methyl coenzyme of cyanocobalamin, vitamin B_{12}). The reaction only occurred under specialised conditions, viz in aqueous solution at pH 1, using Fe(III) or Co(III) as an oxidising agent. No reaction was found to occur between Sn(II) and methylcobalamin in the absence of an oxidising agent nor between Sn(IV) and methylcobalamin under a variety of conditions. Further evidence of the biomethylation of tin comes from the work of Brinckman et al.[6], who found that in the laboratory $SnCl_4$ was converted to dimethyltin dichloride by a strain of Pseudomonas bacteria. The feasibility of methylation of inorganic tin in the environment has recently been reviewed by Craig[7], who concludes that, although there is certain circumstantial evidence for the biological methylation of tin, as yet there is no direct evidence. However, even if it is shown that methylation does occur, the consequences will not be so great if it is also shown that the methyltins degrade in the environment back to inorganic tin with a rate comparable to, or faster than, the methylation process.

2.2. Mechanisms of tin-carbon bond cleavage

Degradation involves the breaking of a Sn-C bond, and it is found that such bond cleavage can occur by any of the following

mechanisms:

a) Ultra-violet (U.V.) irradiation.

U.V. light is that part of the electromagnetic spectrum containing wavelengths in the range 10 nm. - 400 nm. and is immediately to high energy of visible light which extends from approximately 400 nm. - 700 nm. The wavelengths of U.V. light below 200 nm. are, however, absorbed by air and so can only be transmitted in a vacuum.

U.V. light of wavelength 200 nm. possesses an energy of 143.2 kcals mol^{-1} and even blue light at 400 nm. has an energy of 71.6 kcals mol^{-1}. These amounts of energy are sufficient to cause bond cleavage provided that absorption of the light takes place. As such, irradiation with U.V. light can cause Sn-C bond cleavage, since the maximum absorption wavelength of organotin compounds is generally within the U.V. region[8].

Many studies have been made of various photochemical reactions of organotins, but it is only in the last ten years that the emphasis of some work has been placed upon investigating degradation processes. Cenci and Cremonini[9] investigated the rate of disappearance of triphenyltin acetate and triphenyltin hydroxide in different types of soil when exposed to U.V. light, without suggesting what the breakdown products were and Corbin[10] studied the U.V. breakdown of triphenyltin hydroxide, suggesting that dicyclohexyltin, monocyclohexyltin and inorganic tin species were produced, but further details were not given. Akagi and Sakagami[11] irradiated several triphenyl-, dibutyl- and dioctyl-tin compounds on a watch glass and concluded that

they all broke down to inorganic tin. The breakdown of the triphenyltin compounds was suggested to occur stepwise

$$\underline{\text{i.e.}} \quad Ph_3SnX \longrightarrow Ph_2SnX_2 \longrightarrow PhSnX_3 \longrightarrow \text{inorg. Sn.}$$

Barnes et al.[12] showed that triphenyltin acetate was broken down to inorganic tin by U.V. light, while Massaux[13] irradiated triphenyltin chloride on a watch glass with light of wavelengths of 254 nm. and 350 nm., showing breakdown occurred faster at the lower wavelength. A similar study was made by Chapman and Price[14] for triphenyltin acetate. In this case irradiations were carried out using wavelengths greater than 235 nm. and 350 nm. and diphenyl-, monophenyl- and inorganic tin species were quantitatively determined as breakdown products. Again breakdown was shown to occur at a faster rate with lower wavelength light. The U.V.-induced decomposition of bis(tri-n-butyltin) oxide has been studied by Kloetze[15] under a variety of conditions of temperature, irradiation intensity and on different matrices. The same author found[16] that the relative rates of breakdown of tributyltin chloride and bis(tributyltin) oxide were similar, while dibutyltin dichloride broke down faster than dibutyltin oxide. These studies were, however, only concerned with the decomposition of the starting compounds and did not suggest possible breakdown products or follow the reaction through to inorganic tin. The U.V. breakdown of bis(tri-n-butyltin) oxide has also been reported by Popl[17].

The study of the U.V. degradation of organotins in aqueous solution has not received much attention, presumably because their low aqueous solubility makes the analysis particularly difficult.

In a paper reporting the rates of hydrolysis of organotins, Mazaev[18] noted that irradiation of aqueous solutions of diethyltin dicaprylate and dibutyltin bis(S,S'-isooctylthioglycolate) produced an increase in the rate of disappearance of the compounds compared to non-irradiated solutions and Soderquist and Crosby[19] reported the U.V. degradation of triphenyltin hydroxide in water, showing that breakdown to inorganic tin would occur under simulated environmental conditions.

b) Gamma (γ) irradiation.

The reaction of highly energetic particles, such as γ-radiation, with matter is by interaction with the electron shells of molecules. Energy is absorbed and electrons ejected to produce ions. These ions, however, are found to be unstable and decompose with the formation of excited molecules and radicals and it is these species that undergo the reactions accounting for the products that are ultimately observed.

γ- irradiation has been employed for the production of organotin free radicals in electron spin resonance investigations[20], but, with regard to degradation studies, Dunn and Oldfield[21] have investigated the effect of irradiation of butyltins in solution in hexane or benzene, and traces of the stepwise degradation products were detected.

c) Chemical cleavage.

The Sn-C bond is capable of polarisation in either direction, ($Sn(\delta+) - C(\delta-)$ or $Sn(\delta-) - C(\delta+)$),[22] and is, therefore, susceptible to attack by both nucleophilic and electrophilic

reagents. Therefore, for reactions of the type

A-B may be one of a wide variety of compounds, e.g. mineral acids, carboxylic acids, halogens, alkalis etc. As well as polar reactions, free radical processes can cause homolytic Sn-C bond cleavage, the Sn-C bond being a fairly good radical trap[22].

The very wide range of chemical reactions involving Sn-C bond cleavage renders a review outside the scope of this thesis. However, a number of discussions are available[8,22].

d) Biological cleavage.

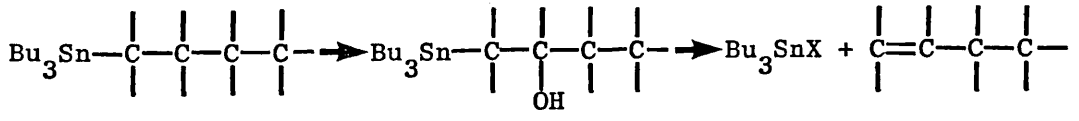
The question of biodegradation of organotins is particularly important in situations where, for example, the breakdown cannot occur due to the action of light, e.g. in the soil.

It has been shown by Barnes et al[12] that ^{14}C labelled - triphenyltin acetate in soil is broken down to inorganic tin. Since carbon dioxide was evolved, and breakdown did not occur in sterile soil it was concluded that degradation was due to the ability of certain microorganisms to metabolise the organotin. Barug and Vonk[23] have shown that bis(tri{1-^{14}C}butyltin) oxide undergoes breakdown in soil, due to the action of microorganisms and it is also reported[24] that tricyclohexyltin hydroxide will break down in soil.

The degradation, in wood, of bis(tri-n-butyltin) oxide has been examined[25] and it was found that the end-product of the

breakdown process appears to be a monobutyltin species. This breakdown process could be due to fungal degradation, since it has been demonstrated that Coniophora cerebella and Polystictus versicolor will degrade bis(tri-n-butyltin) oxide to di- and mono-butyltin species. There is, however, the additional possibility that degradation in wood is due to acid cleavage, because both formic and acetic acids may be present in some types of wood[26].

The metabolic fate of organotins in mammals is also of prime importance. Cremer[27] showed that tetraethyltin is metabolised in vitro and in vivo in rats to a triethyltin species which undergoes further breakdown in vitro to diethyltin derivatives[28]. Diethyltin compounds have also been shown to break down in vivo to monoethyltin derivatives which are eliminated from the body in a short time[29]. These processes are believed to apply to other trialkyltin compounds[28]. Fish et al[30] have shown with butyltin compounds that the primary metabolic reaction is carbon hydroxylation and not Sn-C bond cleavage. Using {1- ^{14}C} tetrabutyltin, an in vitro study[30] revealed the major, primary metabolite to be 2-hydroxybutyltributyltin which underwent a rapid β-elimination to give 1- butene and a tributyltin compound.



A study with tributyltin acetate showed a similar process to occur yielding dibutyltin derivatives[30].

Tricyclohexyltin hydroxide has been found[31] to be metabolised in vivo to inorganic tin via di- and mono-cyclohexyltin intermediates and triphenyltin{^{113}Sn} acetate[30] and triphenyltin{^{113}Sn} chloride[32] have been shown to be metabolised in vivo to yield substantial amounts of di- and mono-butyltin derivatives.

e) Thermal cleavage.

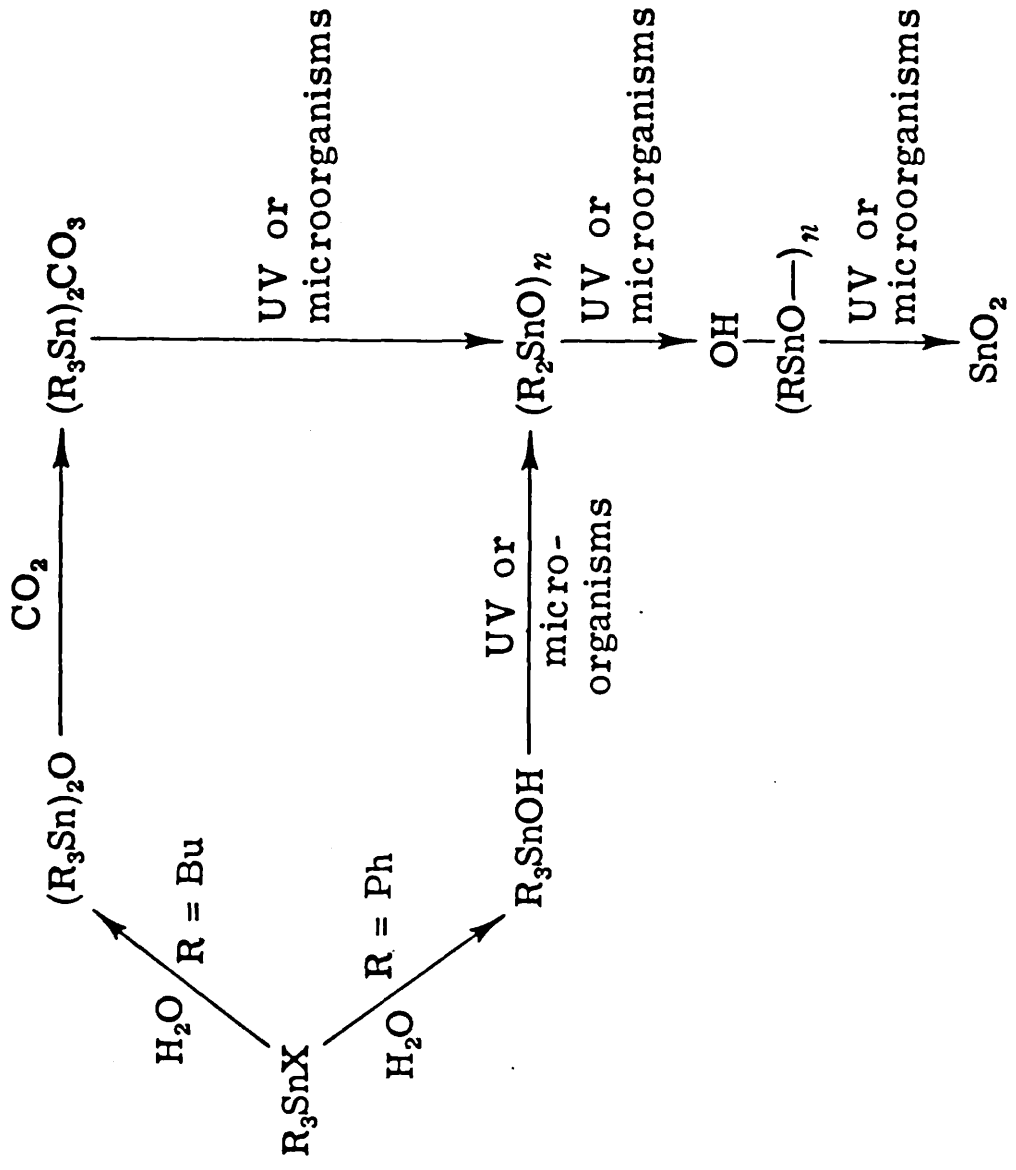
The Sn-C bond may be broken by the action of heat, although it is found that temperatures of over 200^{0}C are required to accomplish this[33].

2.3. Environmental degradation.

Of the various methods discussed for the cleavage of Sn-C bonds, those of γ-irradiation and thermal cleavage may be discounted as far as environmental degradation is concerned, while U.V. irradiation and biological cleavage are probably the most important. A generalised environmental degradation scheme for the commercially used tributyl- and triphenyl-tin derivatives proposed by Sheldon[34] is therefore, illustrated in Figure I. Bis(tributyltin) oxide, formed by hydrolysis of the tributyltin derivative, Bu_3SnX, is shown to first form bis(tributyltin) carbonate since it is known[35] that bis(tributyltin) oxide reacts readily with carbon dioxide. The degradation of all the organotin species in Figure I is suggested as being due to the action of U.V. light or micro-organisms and, of these two degradation mechanisms, it is the former that is the subject of the present investigation. The previous work carried out on the U.V. degradation of organotins (Section 2.2a.) has indicated that breakdown does occur upon irradiation, although very little information is available regarding the reaction mechanisms or the relative rates of breakdown of one organotin compound compared to another. Until such details are known, it will not be possible to select an organotin compound for a particular application, not only on the ability to perform its intended function, but also on whether it will remain stable or degrade in the environment.

FIGURE I

A generalised environmental degradation pattern for triphenyl- and tributyl-tin derivatives[34].


R3SnX
H2O
R = Bu
(R3Sn)2O
CO2
(R3Sn)2CO3
UV or microorganisms
H2O
R = Ph
R3SnOH
UV or micro-organisms
(R2SnO)n
UV or microorganisms
OH
(RSnO—)n
UV or microorganisms
SnO2

2.4. U.V. degradation of organotins.

The U.V. degradation of a compound may be studied in two ways. Firstly, the system may be studied at concentrations which would be encountered in environmental situations, i.e. at the p.p.m. or sub-p.p.m. level, using irradiation intensities which simulate natural sunlight. The second method, involves an investigation of rather concentrated samples with light of high intensity in wavelengths below 300 nm. The first system provides information which is of more general use and of direct interest to the environmentalist. However, the very low concentrations involved give rise to difficulties in analysis. Consequently the mechanistic and kinetic information may be lost and the investigation restricted to saying whether or not breakdown did occur. The second system permits easier analysis. Therefore, more information regarding the species involved in the reaction is likely to be obtained and quantitative measurement of the concentrations of these species with respect to irradiation time is also facilitated. However, results obtained in this manner may not always be directly applicable to the environmental situation and this limitation should be realised. For example, the spectral distribution of the irradiating source may not match that of sunlight, and so reactions which are seen to occur quite rapidly may, in the environment, occur very slowly or perhaps not at all. Furthermore, other effects, such as the concentration of dissolved oxygen in the solution, which may not be important at high concentrations, may affect the reaction at the environmental level.

Due to the difficulties in analysis which arise in the study of degradation at environmental levels it was decided to study systems at relatively high concentrations using N.M.R. spectroscopy as the analytical technique.

The organotin compounds which give rise to the simplest ^{1}H N.M.R. spectra are the methyltins, Me_nSnX_{4-n}, and, since, compounds of the type R_3SnX show the highest biological activity it was decided to study the degradation of trimethyltin chloride. Although trimethyltin compounds have no commercial outlets, certain di- and mono-methyltin derivatives are used industrially (Section 1.4.), and with the concern over the possible methylation of inorganic tin in the environment, the study of the degradation of the methyltins is obviously of importance.

The degradation of compounds exhibiting more complex ^{1}H N.M.R. spectra cannot be studied by the same technique due to the overlapping of closely coupled resonances preventing the analysis of a mixture. ^{1}H decoupled ^{119}Sn F.T.N.M.R. spectra are by comparison very simple and interpretable. Therefore, it was decided to study the U.V. degradation of tributyltin chloride by ^{119}Sn F.T.N.M.R. spectroscopy.

Analysis of the degraded products is made even more simple if the anionic radical X, in R_4SnX_{4-n}, is the same throughout. In addition, if the degradation sequence is to be followed through to inorganic tin the solubility of the products in the solvent medium must be considered. For example, the dialkyltin oxides, $(R_2SnO)_n$, are insoluble in all common solvents and their formation would present problems in studying the degradation process. Thus, carbon tetrachloride was chosen as the solvent for the initial investigations, since most organotins have a good solubility in this solvent. In addition, the degradation products are almost certain to remain as chlorides throughout, and carbon

tetrachloride does not give a signal in the ^{1}H N.M.R. spectrum. However, since carbon tetrachloride is a solvent that would not be encountered in environmental situations, a study of the degradation of trimethyltin chloride in water was also carried out.

The systems studied in this investigation were, therefore, as follows:

The U.V. degradation of

1) the methyltin chlorides in carbon tetrachloride;
2) tributyltin chloride in carbon tetrachloride;
3) trimethyltin chloride in water.

2.4.1. U.V. degradation of the methyltin chlorides in carbon tetrachloride.

In carbon tetrachloride, the methyltin chlorides, Me_nSnCl_{4-n}, exist as non-associated molecules with a tetrahedral geometry. The ^{1}H N.M.R. chemical shifts, δ, and coupling constants, $^{2}J(^{1}H - ^{119}Sn)$ in carbon tetrachloride, of the species are given below and are in agreement with literature values[36]

	δ(p.p.m.)	$J(^{1}H - C - ^{119}Sn)$ (Hz)
Me_3SnCl	0.61	58.1
Me_2SnCl_2	1.15	69.0
$MeSnCl_3$	1.69	100.0

In studying the degradation process, the limits of detection of the analytical technique must first be considered. The minimum concentration of trimethyltin chloride that could be quantitatively determined with the available N.M.R. instrument was found to be 0.005 M. Therefore, it was decided that irradiations would be made upon 0.05 M solutions.

During the degradation of an R_3SnX compound through to inorganic tin it is probable that mixtures of various amounts of R_3SnX, R_2SnX_2, $RSnX_3$ and SnX_4 will be present in solution simultaneously. It is known[37] that, under certain conditions, these compounds undergo various redistribution reactions, e.g.

$$R_3SnX + SnX_4 \longrightarrow R_2SnX_2 + RSnX_3$$

$$R_3SnX + RSnX_3 \longrightarrow 2R_2SnX_2$$

Therefore, the redistribution reactions of the methyltin chlorides and stannic chloride were investigated under similar conditions to those that would be encountered during irradiation. Thus, the following equimolar mixtures (total molarity = 0.05 M) in carbon tetrachloride were prepared and sealed in N.M.R. tubes.

1) Me_3SnCl/Me_2SnCl_2 2) $Me_3SnCl/MeSnCl_3$ 3) $Me_3SnCl/SnCl_4$

4) $Me_2SnCl_2/MeSnCl_3$ 5) $Me_2SnCl_2/SnCl_4$ 6) $MeSnCl_3/SnCl_4$

7) $Me_3SnCl/Me_2SnCl_2/MeSnCl_3$

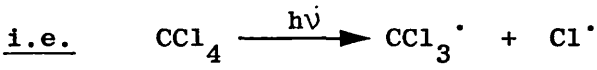
The tubes were kept at 40^0C (the approximate temperature which would be experienced during irradiation) and ^1H N.M.R. spectra of the mixtures were recorded periodically for up to 14 days. In all of the above mixtures, the only reaction that was seen to be occurring was that between trimethyltin chloride and stannic chloride.

i.e. $Me_3SnCl + SnCl_4 \longrightarrow Me_2SnCl_2 + MeSnCl_3$

The rate of this reaction was, however, found to be quite slow, since, after 14 days, approximately 40% of the initial trimethyltin chloride still remained. As such, it was judged that little

or no interference with the degradation reaction would occur from redistribution processes.

A photochemical reaction cannot occur unless absorption of a photon of light takes place. Therefore, the U.V. absorption spectra of the methyltin chlorides in carbon tetrachloride were recorded and all three compounds were found to have an absorption maximum at approximately 260 nm. The intensity of absorption was highest for monomethyltin trichloride and lowest for trimethyltin chloride. The U.V. absorption of carbon tetrachloride was also recorded and it was found that the solvent had a sharp absorption cut off at approximately 230 nm. Since carbon tetrachloride is known to be cleaved homolytically by U.V. light[38],



it was necessary for samples to be irradiated with light of wavelength greater than 235 nm.

Solutions of 0.05 M trimethyltin chloride in carbon tetrachloride were irradiated for increasing periods of time at a fixed distance (intensity of irradiation: 200-300 nm. ≈ 5 mwatts cm^{-2}; 300-400 nm ≈ 7 mwatts cm^{-2}) and were analysed by ^{1}H N.M.R. spectroscopy. Dimethyltin dichloride and methyltin trichloride were determined as degradation products. As results accumulated it became apparent that they covered a wide spread, possibly due to a slight asymmetry of the samples with respect to the light source during irradiation. Thus, each irradiation was repeated a number of times, permitting mean values of the concentration of each species to be calculated, and these results are given in Table I. For the shorter irradiation times the accuracy of the results is reflected not only by the standard deviation of the mean but

TABLE I: Results of the U.V. degradation of Me_3SnCl (0.05 M in CCl_4).

		Me_3SnCl		Me_2SnCl_2		$MeSnCl_3$		TOTAL
t (hrs.)	N	$\overline{A}$ (M)	σ_{N-1}	$\overline{A}$ (M)	σ_{N-1}	$\overline{A}$ (M)	σ_{N-1}	(M)
0.0		0.05	-	-	-	-	-	0.05
0.5	4	.041	.002	0.008	.001	-	-	.049
1.0	4	.034	.002	.014	.001	-	-	.049
1.5	2	.025	.001	.019	.000	-	-	.044
2.0	4	.019	.002	.029	.002	-	-	.048
2.5	4	.016	.001	.035	.003	-	-	.051
3.0	3	.008	.000	.038	.002	0.004	.001	.050
3.5	6	.005	.002	.041	.004	.005	.002	.051
4.0	8	.003	.001	.038	.004	.012	.004	.053
5.0	12	-	-	.032	.003	.018	.003	.050
6.0	6	-	-	.025	.001	.027	.002	.052

TABLE I: Cont'd...2.

t (hrs.)	N	Me_3SnCl $\bar{A}$ (M)	σ_{N-1}	Me_2SnCl_2 $\bar{A}$ (M)	σ_{N-1}	$MeSnCl_3$ $\bar{A}$ (M)	σ_{N-1}	TOTAL (M)
7.0	8	-	-	.019	.006	.029	.005	.048
8.0	8	-	-	.013	.005	.035	.004	.048
9.0	8	-	-	.008	.006	.041	.004	.049
10.0	7	-	-	.005	.005	.042	.004	.047
11.0	8	-	-	-	-	.042	.003	.042
12.0	9	-	-	-	-	.038	.004	.038
13.0	8	-	-	-	-	.037	.004	.037
15.0	8	-	-	-	-	.032	.004	.032
17.0	7	-	-	-	-	.027	.003	.027
20.0	6	-	-	-	-	.019	.002	.019
25.0	7	-	-	-	-	.007	.002	.007

t = irradiation time (hrs.)

N = number of samples irradiated for a given t.

$\bar{A}$ = average concentration (M) of N results.

σ_{N-1} = standard deviation of $\bar{A}$ for N-1 results.

also by checking that the total of the organotin concentrations is determined as being equal to the starting concentration of 0.05 M.

The total tin content of selected samples, particularly of those which had been irradiated for longer periods, was determined by volumetric analysis and was found to remain at 0.05 M. Therefore, since inorganic tin cannot be determined by ^{1}H N.M.R., its presence was shown qualitatively by paper chromatography[39] and its concentration was measured indirectly as the difference between the starting concentration and the total organotin concentration. The concentrations of inorganic tin determined in this manner are given in Table II and the results of Tables I and II are shown in Figure II.

TABLE II: The concentration of inorganic tin with respect to irradiation time, produced from the U.V. degradation of 0.05 M trimethyltin chloride in carbon tetrachloride.

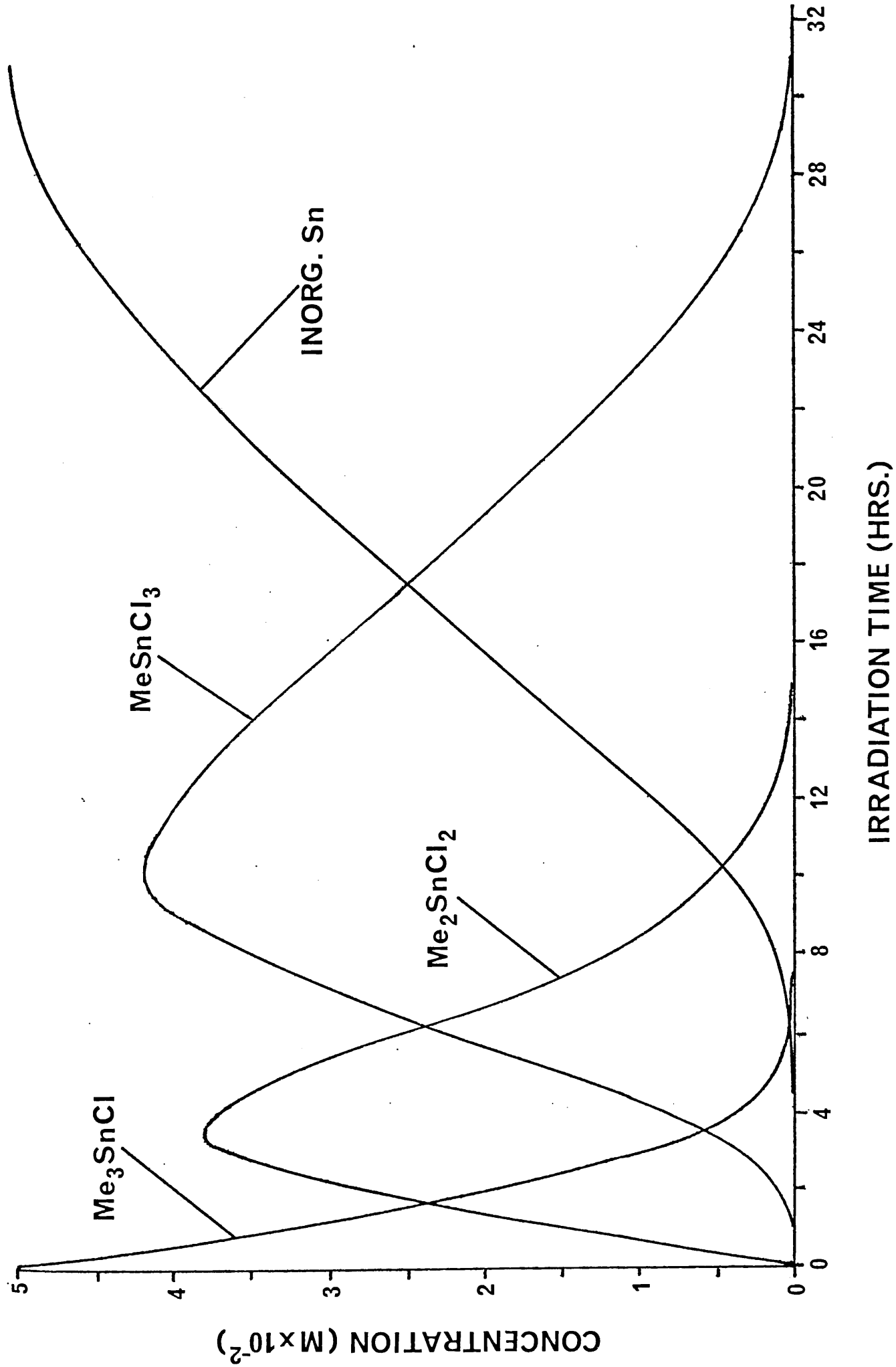
Irradiation time (hrs.)	Inorganic Sn concentration (M)
0	0.00
6	0.001
8	0.002
10	0.003
11	0.006
12	0.009
13	0.012
14	0.016
15	0.019
17	0.024
19	0.029
21	0.034
23	0.039
25	0.044
27	0.047

FIGURE II

The U.V. degradation of 0.05 M trimethyltin chloride in carbon tetrachloride.

Irradiation intensity: 200-300 nm. ≈ 5 mwatts cm^{-2}

300-400 nm. ≈ 7 mwatts cm^{-2}


INORG. Sn
MeSnCl3
Me2SnCl2
Me3SnCl
CONCENTRATION (M x 10-2)
IRRADIATION TIME (HRS.)
0
1
2
3
4
5
0
4
8
12
16
20
24
28
32

From these results it can be clearly seen that trimethyltin chloride in carbon tetrachloride degrades, on irradiation with U.V. light, in a stepwise manner through to inorganic tin.

i.e. $Me_3SnCl \longrightarrow Me_2SnCl_2 \longrightarrow MeSnCl_3 \longrightarrow$ Inorg. Sn

The absorption maximum of the methyltin chlorides in carbon tetrachloride is at 260 nm. and, from the expression

$$E = \frac{Nhc}{\lambda}$$

where N = the Avagadro number, h = Planck's constant, c = velocity of light and λ = wavelength, light of this wavelength is found to possess an energy, E, of 110 kcals mol^{-1}. The mean bond dissociation energies of Sn-Me and Sn-Cl bonds are approximately 52 kcals mol^{-1} and 85 kcals mol^{-1} respectively[22], while a C-H bond has an energy of approximately 98 kcals mol^{-1}.[40] Light with a wavelength of 260 nm., therefore, possesses sufficient energy to cause bond cleavage in the organotin molecule. Thus, it seems that absorption of light leads to cleavage of the Sn-Me bond - the weakest bond in the molecule - and degradation occurs.

In order that the relative rates of breakdown of the methyltin chlorides could be determined 0.05 M solutions of dimethyltin dichloride and methyltin trichloride in carbon tetrachloride were irradiated under the same conditions as the trimethyltin chloride solutions, and were analysed by ^1H N.M.R. Results of these experiments are given in Tables III and IV and a

TABLE III: Results for the U.V. degradation of Me_2SnCl_2 0.05 M in CCl_4.

		Me_2SnCl_2		$MeSnCl_3$		TOTAL
t (hrs.)	N	$\bar{A}$ (M)	σ_{N-1}	$\bar{A}$ (M)	σ_{N-1}	(M)
0		.050		-		.050
1	6	.041	.002	.008	.002	.049
2	6	.032	.002	.018	.001	.050
3	4	.024	.001	.025	.002	.049
4	4	.018	.001	.031	.001	.049
5	4	.015	.001	.034	.002	.049
6	4	.009	.002	.039	.001	.048
7	4	.006	.002	.04	.002	.046
8	4	.004	.002	.043	.001	.047

TABLE IV: Results for the U.V. degradation of $MeSnCl_3$ 0.05 M in CCl_4.

		$MeSnCl_3$	
t (hrs.)	N	$\bar{A}$ (M)	σ_{N-1}
0		.050	
2	4	.043	.001
3	3	.042	.005
4	4	.036	.001
6	4	.027	.002
8	4	.024	.002
10	4	.016	.002
12	4	.009	.003
14	4	.006	.001

t = irradiation time.

N = number of samples irradiated.

$\bar{A}$ = average concentration.

σ_{N-1} = standard deviation of $\bar{X}$ for N-1 results.

plot of the individual breakdown of all the organotins is shown in Figure III. From these results it can be seen that the relative rates of breakdown of the methyltin chlorides, in this system, are as follows:

$$Me_3SnCl > Me_2SnCl_2 > MeSnCl_3$$

This trend in rates is as expected from Figure I, since for a species to accumulate its rate of breakdown must be slower than its rate of formation. In order to obtain an approximation of how much faster one methyltin species degrades compared to another, it was decided to try to assign the best first order fit to the experimental results. Since a plot of $\ln(A_o/A)$ vs t, where A is the concentration of the organotin and t the irradiation time, did not yield a straight line, an approximation to the relative rates of breakdown was found by fitting what was visually judged to be the best exponential curve to the experimental results, as illustrated in Figures IV, V and VI. Comparison of the constants, K, which generate such exponential curves gives an approximation of the relative rates of breakdown, and such values of K for each of the three organotin species are given below.

	K (hr^{-1})
Me_3SnCl	0.540
Me_2SnCl_2	0.252
$MeSnCl_3$	0.105

Therefore, it may be said that the approximate relative rates of breakdown of the methyltin chlorides in carbon tetrachloride are as follows:

The rate of breakdown of Me_3SnCl is approximately 2 times the rate of breakdown of Me_2SnCl_2

FIGURE III

The relative U.V. degradation of trimethyltin chloride, dimethyltin dichloride and methyltin trichloride (0.05 M in carbon tetrachloride).

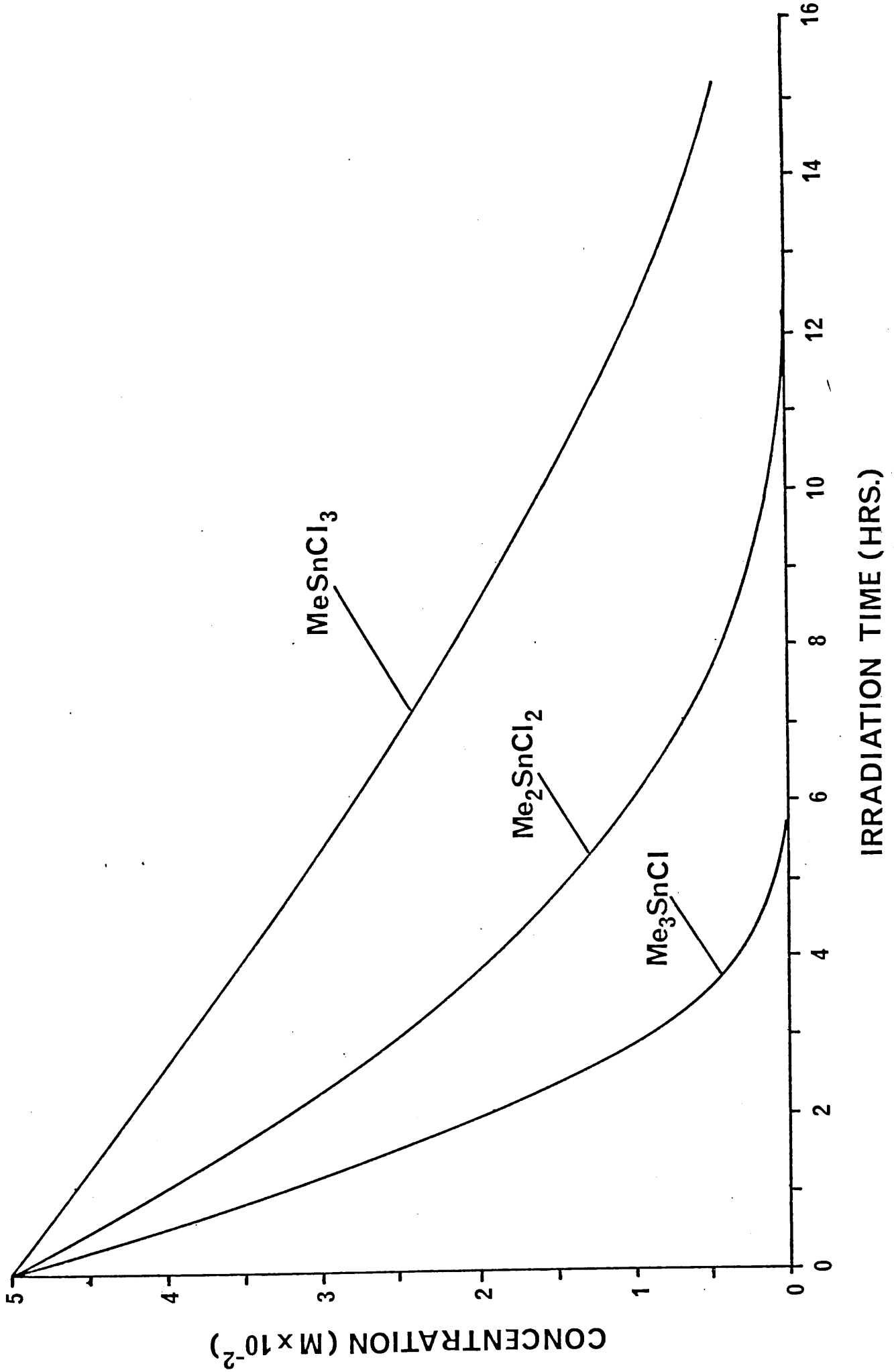

CONCENTRATION (M x 10-2)
IRRADIATION TIME (HRS.)
MeSnCl3
Me2SnCl2
Me3SnCl
0
1
2
3
4
5
0
2
4
6
8
10
12
14
16

FIGURE IV

A comparison of experimental results and a theoretical first order reaction for the U.V. degradation of Me_3SnCl (0.05 M in CCl_4)

1st. order reaction: $A = A_0e^{-kt}$

$A = 0.05$ M, $K = 0.54$ hr^{-1}.

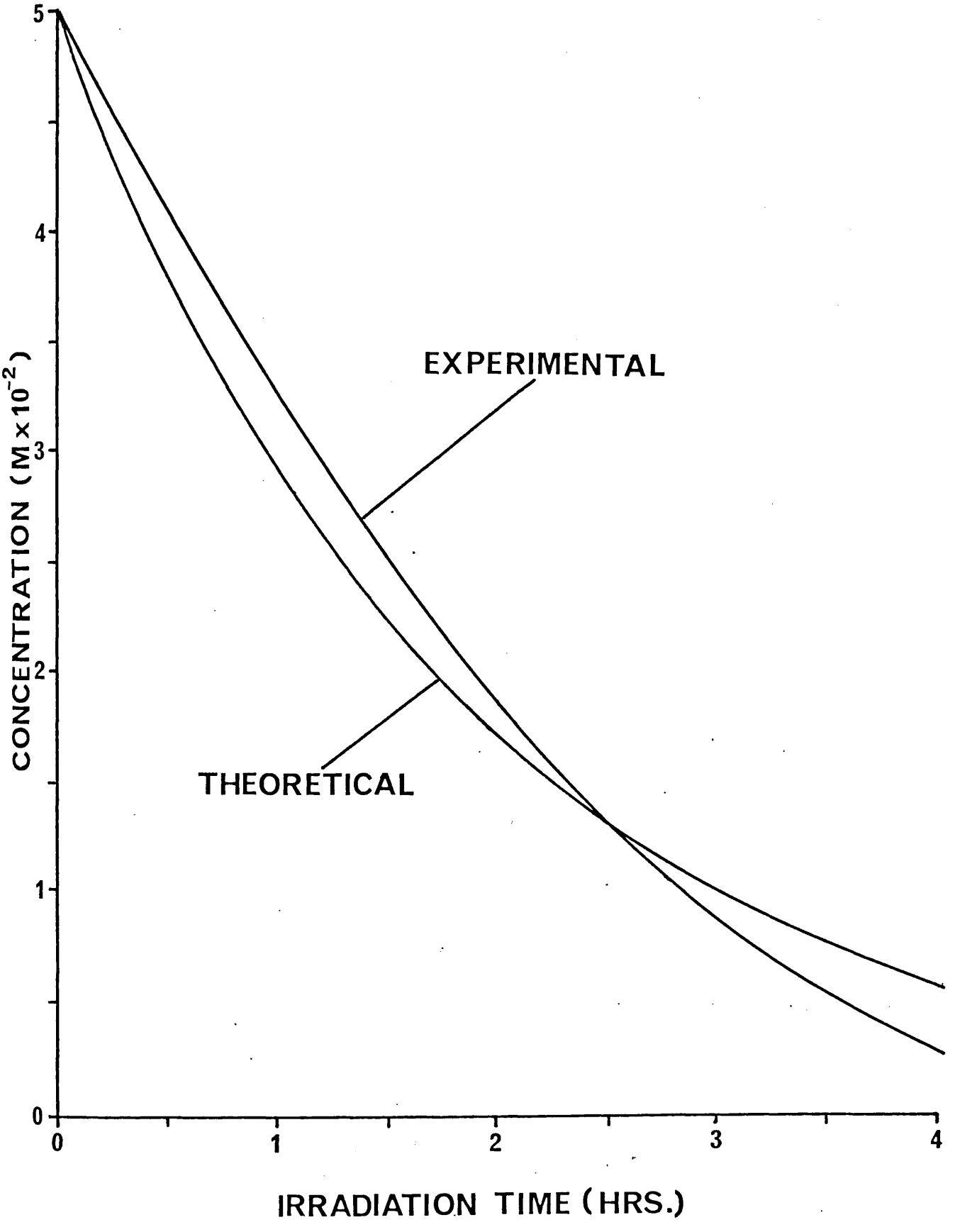

5
4
3
2
1
0
CONCENTRATION (M x 10^{-2})
EXPERIMENTAL
THEORETICAL
0
1
2
3
4
IRRADIATION TIME (HRS.)

FIGURE V

A comparison of experimental results and a theoretical first order reaction for the U.V. degradation of Me_2SnCl_2 (0.05 M in CCl_4)

1st. order reaction: $A = A_0e^{-kt}$

A_0 = 0.05M, K = 0.252 hr^{-1}.

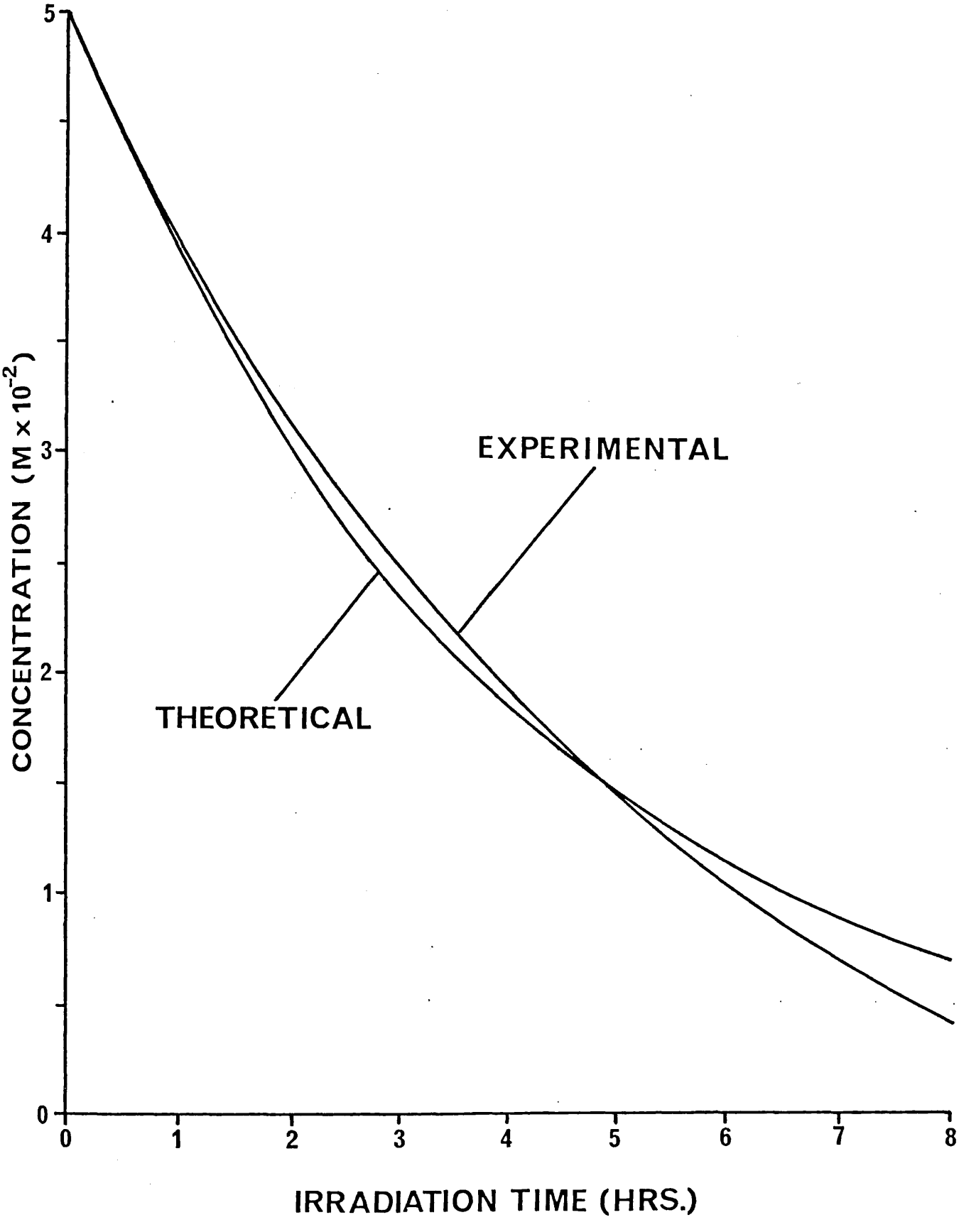
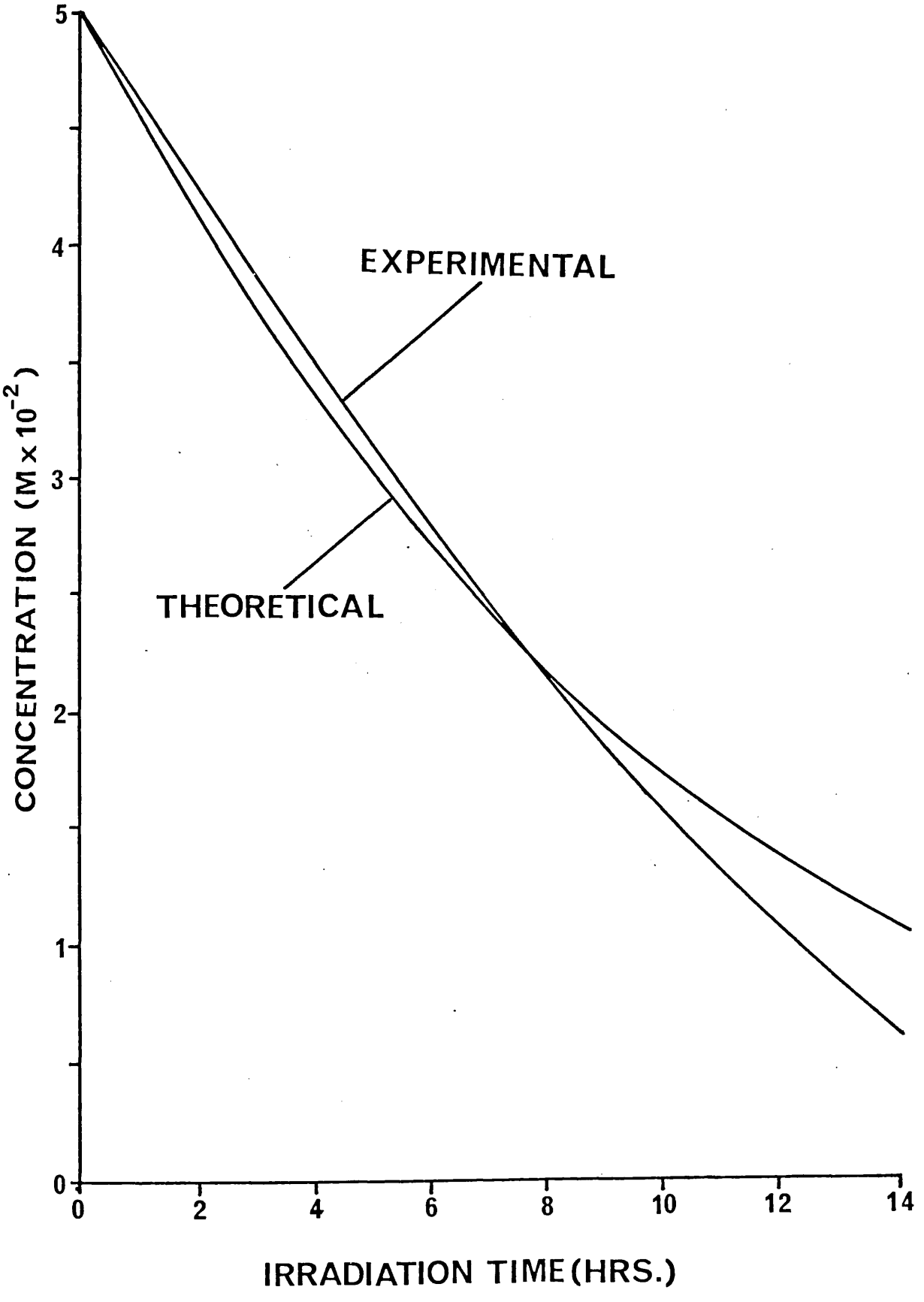

5
4
3
2
1
0
CONCENTRATION (M x 10^{-2})
EXPERIMENTAL
THEORETICAL
0
1
2
3
4
5
6
7
8
IRRADIATION TIME (HRS.)

FIGURE VI

A comparison of experimental results and a theoretical first order reaction for the U.V. degradation of $MeSnCl_3$ (0.05M in CCl_4)

1st. order reaction: $A = A_0 e^{-kt}$

A_0 = 0.05M, K = 0.105 hr^{-1}.


5
4
3
2
1
0
CONCENTRATION (M x 10^{-2})
EXPERIMENTAL
THEORETICAL
0
2
4
6
8
10
12
14
IRRADIATION TIME (HRS.)

The rate of breakdown of Me_3SnCl is approximately 5 times the rate of breakdown of $MeSnCl_3$.

It was considered of interest to compare the results shown in Figure II with results which would be obtained for a totally theoretical series first-order reaction of the form:

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C \xrightarrow{K_3} D$$

If A_o is the concentration of A at time, t = O, and

$$A_o = A + B + C + D$$

the rates of reaction may be represented by

$$\frac{dA}{dt} = -K_1A \qquad 1$$

$$\frac{dB}{dt} = K_1A - K_2B \qquad 2$$

$$\frac{dC}{dt} = K_2B - K_3C \qquad 3$$

$$\frac{dD}{dt} = K_3C \qquad 4$$

Equation 1 readily integrates to give

$$A = A_o e^{-K_1 t}$$

and substitution into equation 2 gives

$$\frac{dB}{dt} = K_1 A_o e^{-K_1 t} - K_2B$$

This linear first order equation may be integrated by the

integrating factor method[41] to give

$$B = A_o \frac{K_1}{K_2 - K_1} (e^{-K_1 t} - e^{-K_2 t})$$

Similarly an expression for C may be obtained

$$C = A_o \frac{K_2 K_1}{K_2 - K_1} \left[\frac{1}{K_3 - K_1} (e^{-K_1 t} - e^{-K_3 t}) + \frac{1}{K_3 - K_2} (e^{-K_3 t} - e^{-K_2 t}) \right]$$

The concentration of D is given, simply, by

$$D = A_o - A - B - C.$$

Hence if A = Me_3SnCl, B = Me_2SnCl_2, C = $MeSnCl_3$ and D = inorganic tin, and if K_1 = 0.54 hr^{-1}, K_2 = 0.252 hr^{-1} and K_3 = 0.105 hr^{-1}, substitution into the above expressions for A, B, C and D gives the theoretical breakdown procedure, illustrated in Figure VII. Comparison of Figures II and VII shows that, although the overall basic shape is similar, differences are present, in particular the maximum concentrations of Me_2SnCl_2 (B) and $MeSnCl_3$ (C). These differences are most certainly due to the fact that the degradation procedure is more complicated than may be represented by a first-order expression. Attempts were made to improve the theoretical fit by taking different values of K_1, K_2 and K_3, but no improvement occurred, and substitution of experimental values of Me_3SnCl (A), followed by theoretical calculation of B, C and D gave only a very slight improvement.

FIGURE VII

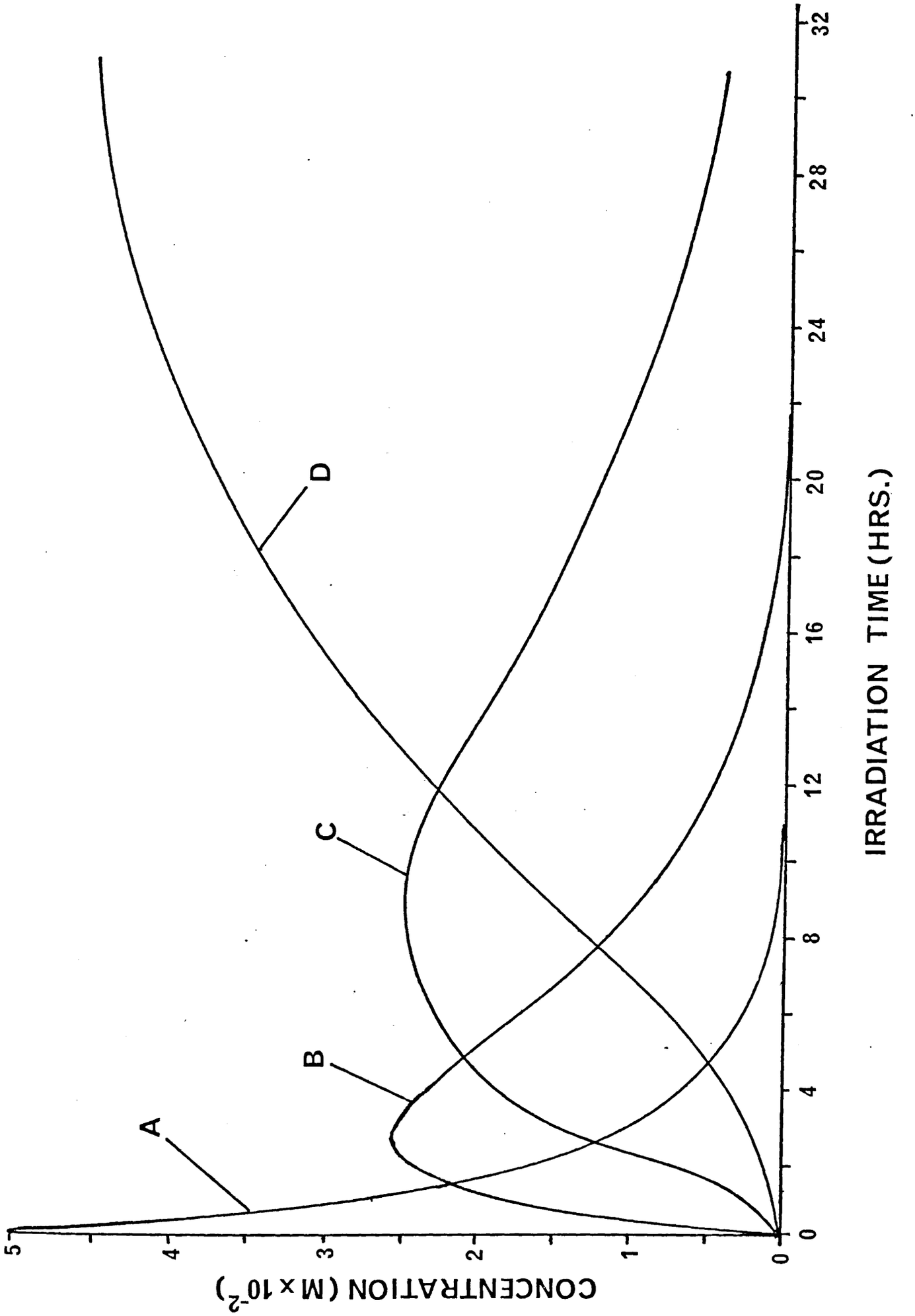
A theoretical first-order reaction of the type

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C \xrightarrow{K_3} D$$

$K_1 = 0.54\ hr^{-1}$

$K_2 = 0.252\ hr^{-1}$

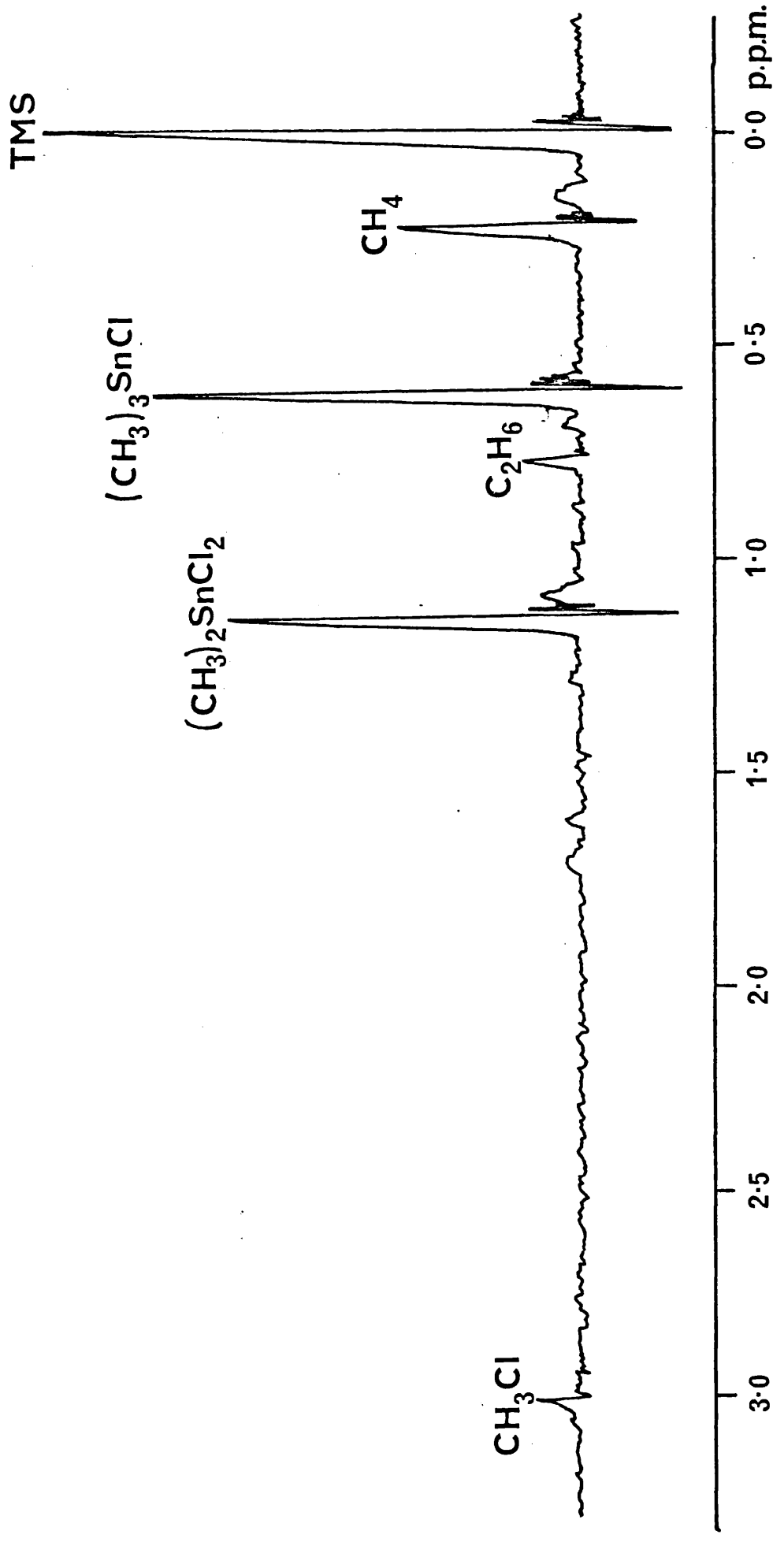
$K_3 = 0.105\ hr^{-1}$


CONCENTRATION (M x 10⁻²)
IRRADIATION TIME (HRS.)
A
B
C
D
0
1
2
3
4
5
0
4
8
12
16
20
24
28
32

The results presented so far were all obtained from irradiation, of solutions in unsealed silica cells, and apart from identification of the organotin degradation products, no other species were detected by ^{1}H N.M.R. Therefore, the non-tin containing products of the degradation reactions must have a very low solubility in carbon tetrachloride and as such are being evolved from solution, preventing detection. Therefore, 0.05 M solutions of trimethyltin chloride in carbon tetrachloride were irradiated in sealed silica 5 mm N.M.R. tubes. The tubes were filled virtually to the top, leaving as little headspace as possible, thereby ensuring that any volatile materials would have a greater chance of remaining in solution. Subsequent analysis of these solutions revealed that the major non-tin containing product of the degradation procedure was methane (CH_4: $\delta^{1}H$ = 0.23 p.p.m.)[42], see Figure VIII. This is perhaps surprising when the molarity of the organotin, 0.05 M, is compared to the molarity of the solvent, ~ 10 M (a 200 times excess). It would be expected that a methyl group formed by cleavage of an Sn-C bond would react with the solvent forming methyl chloride. However, this is not the case and it seems that hydrogen abstraction from a methyl group attached to the organotin occurs and methane is produced. The formation of alkanes from the U.V. irradiation of tetraorganotins in carbon tetrachloride has been observed by Razuvaev *et al*[38], who found that the photochemical reaction of tetraethyltin with carbon tetrachloride in approximately equimolar ratios produced ethane, whereas with the solvent in a molar excess of 4:1 the reaction produced predominantly ethyl chloride. With tetrapropyltin in carbon tetrachloride (molar ratio 1:4), it was observed that the formation of propane but not propyl chloride occurred and, with tetramethyltin, both methane and methyl chloride were produced. The present results of the irradiation of trimethyltin chloride

FIGURE VIII

A ^1H N.M.R. spectrum of a 0.05 M solution of Me_3SnCl, in CCl_4, which has been irradiated for 10 hrs. in a sealed silica tube.


TMS
$(CH_3)_3SnCl$
$(CH_3)_2SnCl_2$
CH_4
C_2H_6
CH_3Cl
0·0 p.p.m.
0·5
1·0
1·5
2·0
2·5
3·0

in carbon tetrachloride showed methane to account for between 55-65% of the total number of Sn-C bonds cleaved. Therefore, hydrogen abstraction from the organotin by a methyl group appears to be a much more favoured reaction than was suggested by the work of Razuvaev[38]. Methyl chloride (CH_3Cl: δ^1H = 3.06 p.p.m.)[43] and ethane (C_2H_6: δ^1H = 0.86 p.p.m.)[42] were also detected in the solutions irradiated in sealed tubes but in lesser amounts.

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

$$Me_3SnCl \xrightarrow{h\nu} Me_2Sn^{\cdot}Cl + Me^{\cdot}$$

$$Me_2Sn^{\cdot}Cl + CCl_4 \longrightarrow Me_2SnCl_2 + CCl_3^{\cdot}$$

$$2\ CCl_3^{\cdot} \longrightarrow C_2Cl_6$$ [38]

Since CH_4 is the predominant non-tin containing product

$$Me^{\cdot} + Me_3SnCl \longrightarrow CH_4 + Me_2\underset{\displaystyle CH_2^{\cdot}}{\underset{|}{Sn}}Cl$$

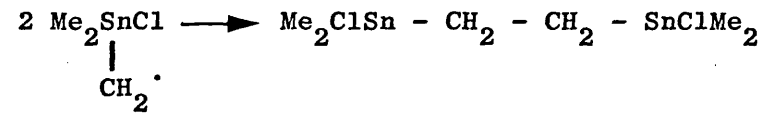
and the only other non-tin containing products presumably arise from

$$Me^{\cdot} + CCl_4 \longrightarrow CH_3Cl + CCl_3^{\cdot}$$

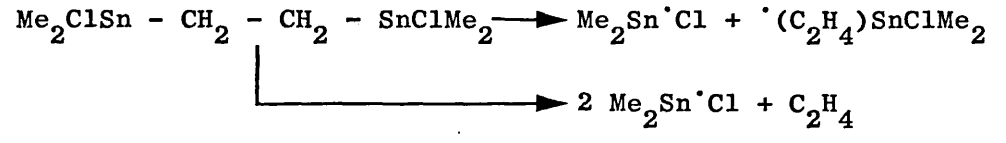
and $2\ Me^{\cdot} \longrightarrow C_2H_6$

It is not known, for certain, what happens to the organotin radical species formed after abstraction of a hydrogen atom.

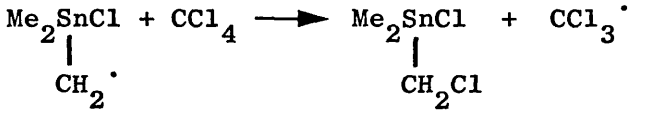
This species could possibly dimerise.



If this reaction occurs the product might not be detected, owing to further degradation taking place



However, at some stage ethylene or ethyl chloride should be present from these reactions, but these products have not been found. Another possibility is the reaction of the organotin radical with the solvent



Again, such an organotin species would be difficult to detect, since it too is probably undergoing further degradation and so will not accumulate. In this case, cleavage of the $-CH_2Cl$ group from tin would, by further hydrogen abstraction, lead to the formation of CH_3Cl, - a species which has been detected in small amounts.

Whatever, the fate of the organotin radical, it can be seen that the overall degradation reaction is rather more complex than light-induced Sn-Me bond cleavage alone and, therefore, it is not surprising that the assumption that the reaction kinetics were first-order, did not give a perfect approximation to the experimental results. Furthermore, it should be realised that,

although the reaction mechanisms discussed above have only involved a trimethyltin species, similar reactions will be occurring simultaneously for the dimethyltin and monomethyltin degradation products.

Finally the possibility of the solvent having an effect on the degradation must be considered. It has been mentioned that carbon tetrachloride undergoes homolytic C-Cl bond cleavage, due to irradiation with U.V. light and that, to minimise this effect, samples were irradiated with light of wavelength greater than 235 nm. However, it is possible that some C-Cl bond cleavage in the solvent could still have been occurring, leading to other possible degradation mechanisms involving direct substitution by radicals arising from the solvent

$$\underline{\text{e.g.}} \quad CCl_4 \xrightarrow{h\nu} CCl_3^{\bullet} + Cl^{\bullet}$$

$$Me_3SnCl + Cl^{\bullet} \longrightarrow Me_2SnCl_2 + Me^{\bullet}$$

If the rate of breakdown was not governed by the intensity of irradiation it would be possible to obtain an indication of the effect of the solvent by studying the breakdown at different concentrations. However, the rate of degradation is found to be dependent upon the intensity of irradiation. At the sample position, the irradiation intensity, of wavelengths between 200 nm. - 300 nm., was measured to be 5 mwatts cm^{-2}. The maximum absorption wavelength of the methyltin chlorides in carbon tetrachloride is 260 nm., and the energy, E, of a single photon of this wavelength may be calculated from

$$E = \frac{hc}{\lambda} \quad \Rightarrow \quad E\ (260\ nm.) = 1.8 \times 10^{-19}\ \text{cals.}$$

If it is assumed that all of the light emitted between 200 nm. - 300 nm. has a wavelength of 260 nm., the number of photons irradiating 1 cm^{-2} of the sample per second may be calculated.

$$\text{No. of photons} = \frac{\text{Irradiation intensity}}{\text{Energy per photon}} \; cm^{-2} \; sec^{-1}.$$

$$= 6.5 \times 10^{15} \; cm^{-2} \; sec^{-1}.$$

A 0.05 M solution contains approximately 3×10^{19} molecules cm^{-3}. Therefore, if the pathlength through the sample was 1 cm, and if every photon was absorbed, it would require approximately 1.5 hours of irradiation to provide sufficient photons to react with all of the organotin molecules.

Consequently, if the initial concentration was doubled, a rate constant representing the breakdown process, found, as before, by taking the best exponential fit to experimental results, would be expected to be approximately halved. Unfortunately, this was not checked by irradiating samples with the original U.V. source, but 0.1 M and 0.05 M solutions of trimethyltin chloride in carbon tetrachloride were irradiated with a new U.V. source, emitting wavelengths upwards of 200 nm. The intensities of irradiation at the sample position (previous intensities are given, for comparison, in parentheses) were measured to be: 200-300 nm. = 4 (5) mwatts cm^{-2}; 300-400 nm. = 7 (7) mwatts cm^{-2}. Irradiated solutions were analysed by ^1H N.M.R. spectroscopy and the results are given in Table V and illustrated in Figure IX. By taking the best exponential fit to the experimental results, rate constants for the degradation of the 0.05 M and 0.1 M solutions were found to be 0.82 hr^{-1} and 0.42 hr^{-1} respectively. (See Figure IX). Therefore, it is seen

TABLE V: U.V. degradation of 0.05 M and 0.1 M solutions of Me_3SnCl in CCl_4, with light of wavelength greater than 200 nm.

Initial concentration (M)	Irradiation time (hrs)	Conc. of Me_3SnCl (M)
0.05	0	0.05
	0.5	0.036
	1.0	0.022
	1.3	0.014
0.1	0	0.1
	0.5	0.085
	1.0	0.072
	2.0	0.045
	2.5	0.034
	3.0	0.023

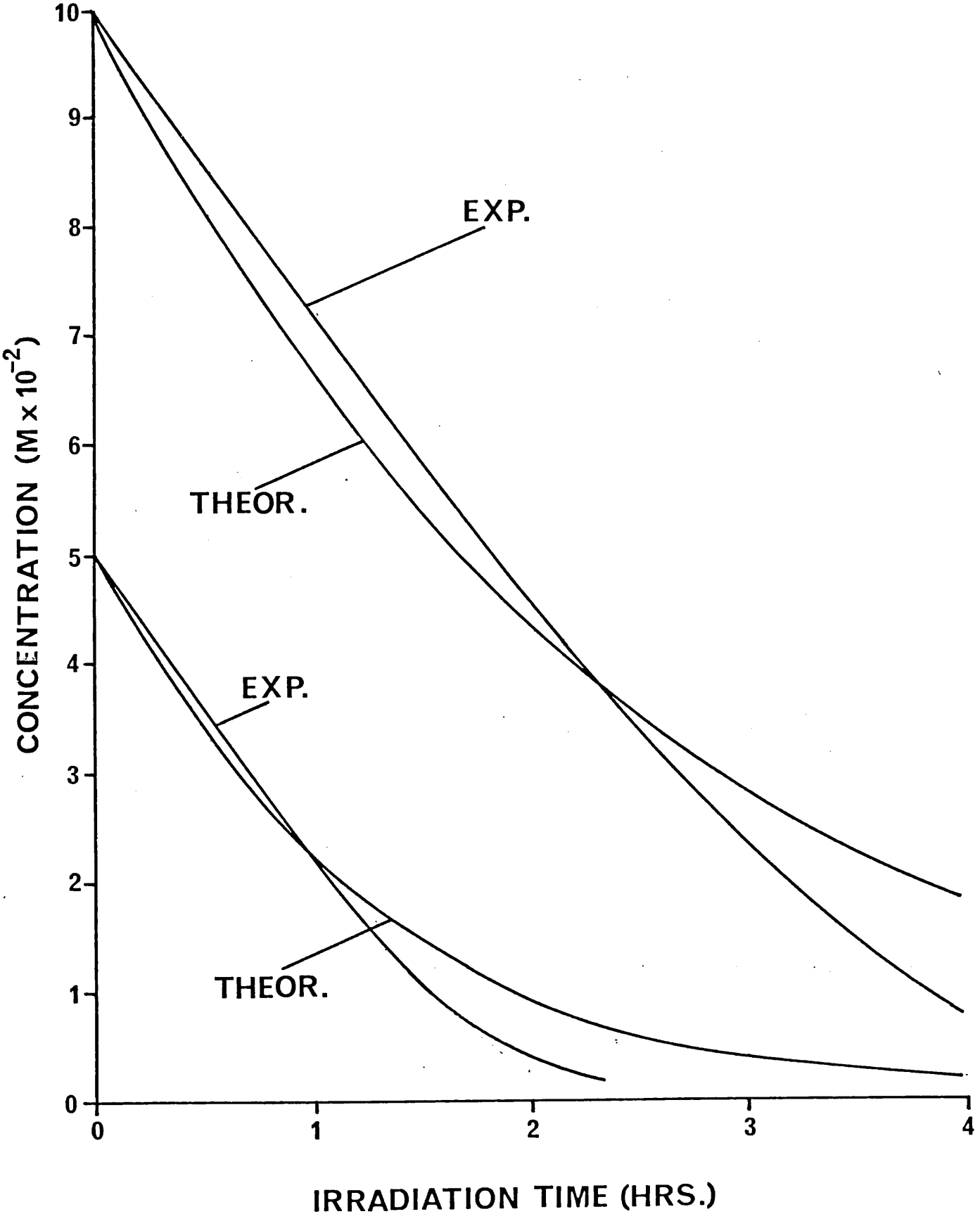
FIGURE IX

A comparison of experimental results and theoretical first order reactions for the U.V. degradation of Me_3SnCl

1st. order reaction $A = A_0 e^{-Kt}$

$A = 0.05$ M $\quad\quad$ $K = 0.82\ hr^{-1}$

$A = 0.10$ M $\quad\quad$ $K = 0.42\ hr^{-1}$


CONCENTRATION (M x 10^{-2})
10
9
8
7
6
5
4
3
2
1
0
EXP.
THEOR.
EXP.
THEOR.
0
1
2
3
4
IRRADIATION TIME (HRS.)

that, as expected, doubling the starting concentration effectively halves the rate constant, i.e. approximately the same quantity of organotin is degrading within a given period of time.

It should be noted that, although the overall irradiation intensities for wavelengths of light greater than 200 nm. were similar to previous irradiations with wavelengths upwards of 235 nm., the degradation occurred at a faster rate with the lower wavelength light. This is possibly due to the action of U.V. light on the solvent, the radicals so produced by the lower wavelengths causing breakdown of the organotin.

2.4.2. U.V. degradation of tri-n-butyltin chloride in carbon tetrachloride.

The ^{1}H N.M.R. spectrum of an equimolar solution of tri-n-butyltin chloride, di-n-butyltin dichloride and n-butyltin trichloride in carbon tetrachloride (Figure X), unlike that of the methyltin chlorides, is very complex due to the overlapping of coupled resonances. This complexity means that quantitative measurement of any one of the compounds in the presence of an excess of the other two would be impossible and so ^{1}H N.M.R. is not a suitable analytical technique for studying the degradation of the butyltin chlorides. The ^{1}H - decoupled ^{13}C N.M.R. spectrum of a similar solution (Figure XI) is far simpler, but still the proximity of the carbon resonances would make quantitiative measurements difficult. However, the ^{1}H - decoupled ^{119}Sn N.M.R. spectrum of a mixture of the butyltin chlorides. (Figure XII) is, by comparison, very simple and easy to

FIGURE X

^{1}H N.M.R. spectrum of a mixture of n-Bu_3SnCl, n-Bu_2SnCl_2 and n-$BuSnCl_3$ in carbon tetrachloride.

^{1}H N.M.R. SPECTRUM OF A MIXTURE OF $BuSnCl_3$, Bu_2SnCl_2 and Bu_3SnCl (0·5M) IN CCl_4

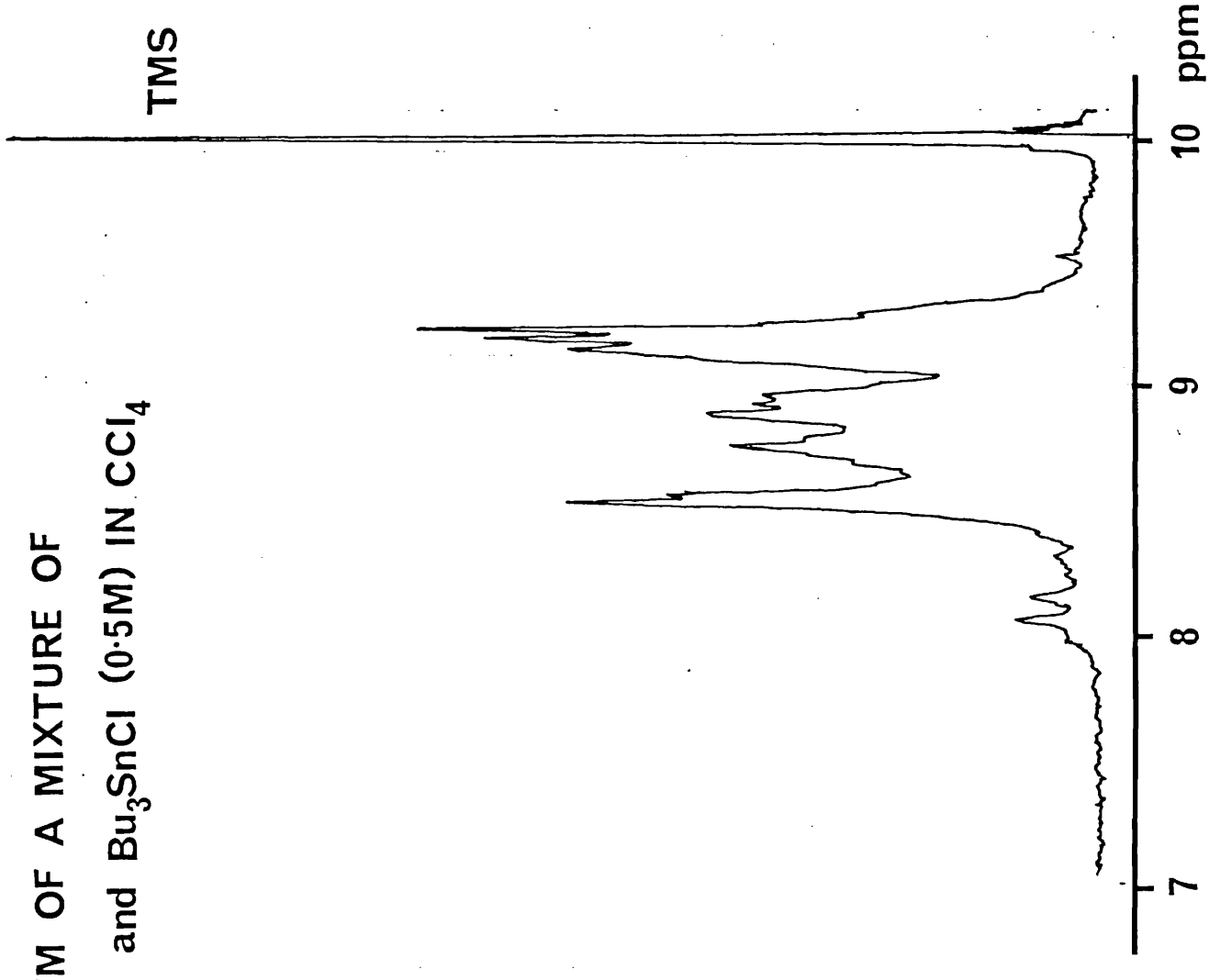


FIGURE XI

^{13}C F.T.N.M.R. spectrum of a mixture of n-Bu_3SnCl, n-Bu_2SnCl_2 and n-$BuSnCl_3$ in carbon tetrachloride.

^{13}C chemical shifts, δ, relative to T.M.S.

Compound	δ (C_α)	δ (C_β)	δ (C_δ)	δ (C_δ)
Bu_3SnCl	33.7	26.7	25.4	13.1
Bu_2SnCl_2	27.0	27.0	26.3	13.5
$BuSnCl_3$	17.0	27.7	26.6	13.4

A MIXTURE OF 0·5M

$BuSnCl_3$, Bu_2SnCl_2, and Bu_3SnCl IN CCl_4

(No. transients = 1280, acquisition time = 1·023 sec.)

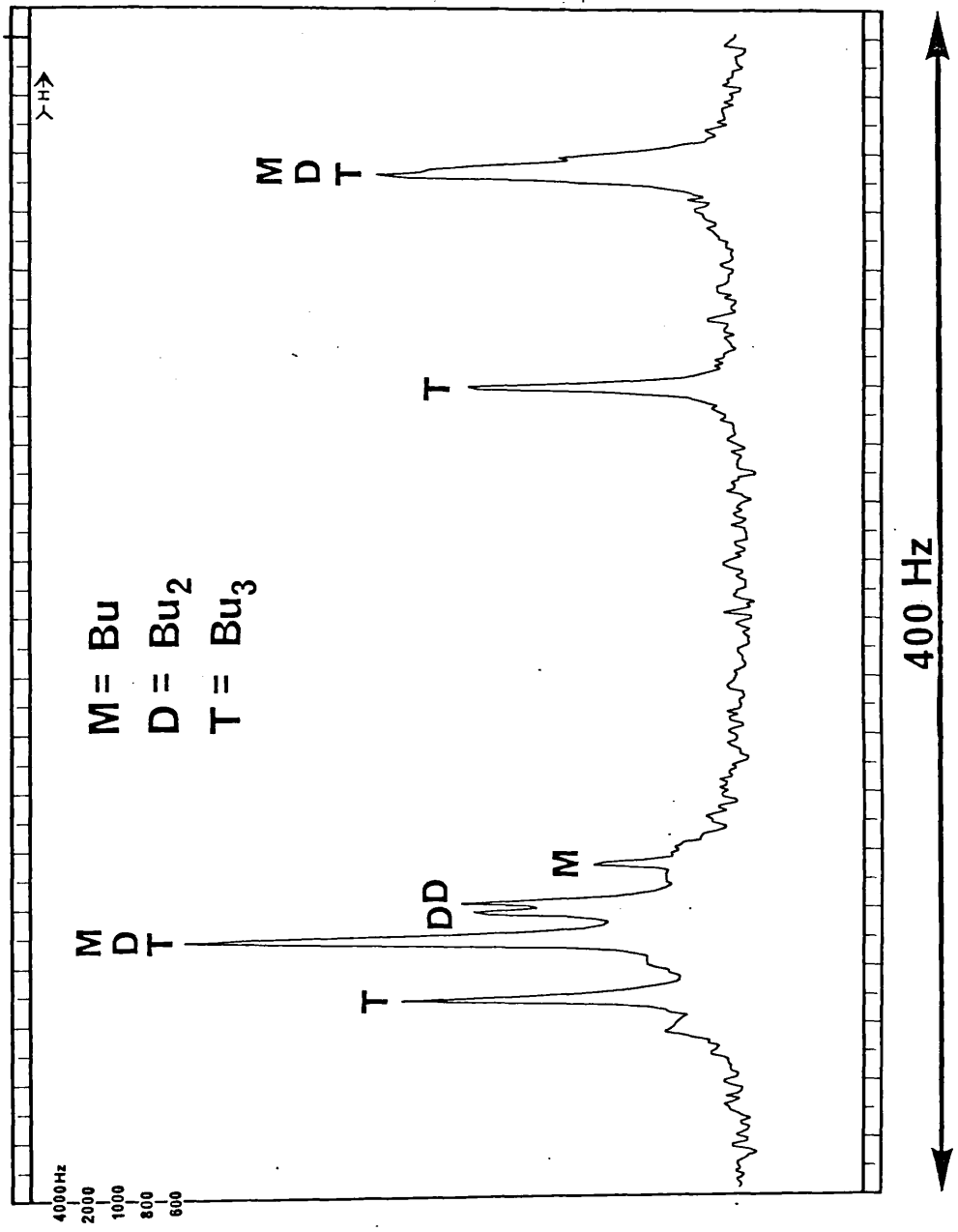
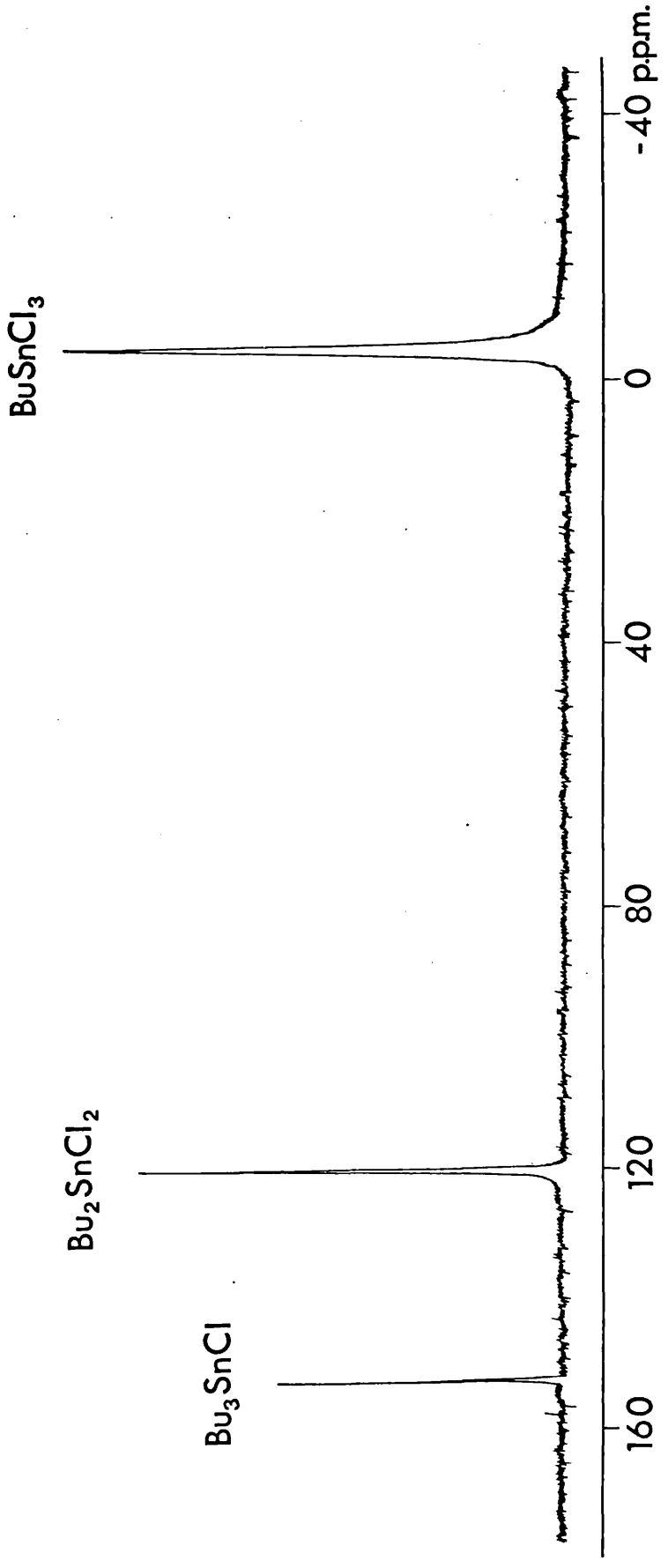


FIGURE XII

^{119}Sn F.T.N.M.R. spectrum of a mixture of n-Bu_3SnCl, n-Bu_2SnCl_2 and n-$BuSnCl_3$ in carbon tetrachloride.

	$\delta\ ^{119}Sn$ (p.p.m.)[a]
n-Bu_3SnCl	+ 151.6
n-Bu_2SnCl_2	+ 120.4
n-$BuSnCl_3$	- 2.8

[a] Relative to Me_4Sn.


BuSnCl3
Bu2SnCl2
Bu3SnCl
-40 p.p.m.
0
40
80
120
160

interpret, the three resonances being rather well separated. It can be seen from Figure XII that the linewidth of the ^{119}Sn resonance increases on going from tributyltin chloride to butyltin trichloride. This is presumably due to the quadrupolar broadening effect of the chlorine atoms attached to tin.

The simplicity of the ^{119}Sn N.M.R. spectrum of the butyltin chlorides would permit easy identification and determination of the breakdown products of tributyltin chloride and so the U.V. degradation study, in carbon tetrachloride, was made using ^{119}Sn F.T.N.M.R. as the analytical technique. Unfortunately, the sensitivity of ^{119}Sn N.M.R. is less than that of ^{1}H N.M.R.[44] and it was therefore not possible to investigate the degradation process at as low a concentration as was used for the methyltin chlorides. It was established that a suitable starting concentration for the degradation study would be 1.5M.

It has been shown[37] that the reaction

$$Bu_3SnCl + BuSnCl_3 \longrightarrow 2\ Bu_2SnCl_2$$

is very slow except at a temperature of at least 200°C. Consequently, unless a situation occurred during the degradation process whereby tributyltin chloride and inorganic tin were present simultaneously,

$$\underline{\text{i.e.}}\ Bu_3SnCl + SnCl_4 \longrightarrow Bu_2SnCl_2 + BuSnCl_3$$

redistribution reactions would not markedly affect the breakdown species and so could be disregarded.

The butyltin chlorides in carbon tetrachloride all absorb U.V. light with a maximum absorption wavelength of 260 nm. Irradiation

was, therefore, carried out using U.V. light of wavelengths above 235 nm.; the intensity of irradiation at the sample position being measured to be 7.5 mwatts cm^{-2} between 200-400 nm. Samples of 1.5 M tributyltin chloride in carbon tetrachloride, contained in silica cells, were irradiated for increasing periods of time and analysed by ^{119}Sn F.T.N.M.R. spectroscopy. The results of which are given in Table VI and shown in Figure XIII.

Table VI: Results of the U.V. degradation of 1.5 M tributyltin chloride in carbon tetrachloride.

Irradiation time (hrs.)	Concentration of Bu_3SnCl (M)	Concentration of Bu_2SnCl_2 (M)
0	1.5	0.0
5	1.1	0.2
10	0.9	0.4
20	0.6	0.6
30	0.6	0.8
50	0.3	0.9

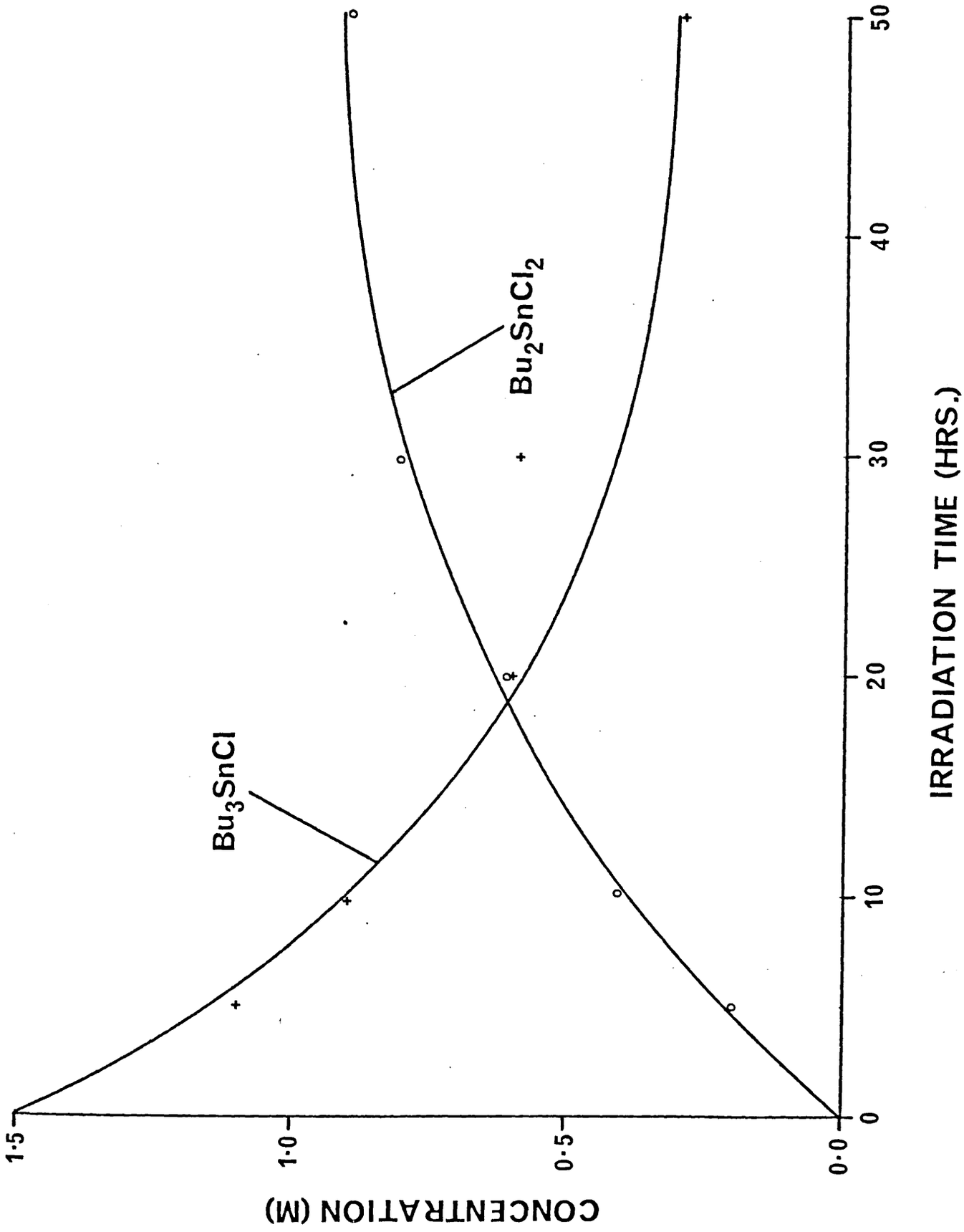
The results show a decrease in the concentration of tributyltin chloride with respect to the irradiation time and the formation of dibutyltin dichloride presumably from:

$$Bu_3SnCl \xrightarrow{h\nu} Bu_2Sn^{\cdot}Cl + Bu^{\cdot}$$

$$Bu_2Sn^{\cdot}Cl + CCl_4 \longrightarrow Bu_2SnCl_2 + CCl_3^{\cdot}$$

FIGURE XIII

The U.V. degradation of a 1.5 M solution of $\underline{n}$-Bu_3SnCl in CCl_4.


CONCENTRATION (M)
1·5
1·0
0·5
0·0
0
10
20
30
40
50
IRRADIATION TIME (HRS.)
Bu_3SnCl
Bu_2SnCl_2

No other products were identified from the ^{119}Sn N.M.R. spectra of the solutions described in Table VI, but irradiation of a 1.5 M solution of dibutyltin dichloride in carbon tetrachloride and subsequent analysis by ^{119}Sn F.T.N.M.R. revealed the presence of butyltin trichloride. Thus, it would seem that the breakdown of tributyltin chloride in carbon tetrachloride is a stepwise process through to inorganic tin.

During irradiation, the colour of the solutions gradually darkens, until after about 50 hours a very small quantity of a brown viscous liquid could be seen to have separated from the solvent. It is well known that colouration can occur due to the formation of conjugated carbon-carbon double bonds in thermally degraded P.V.C.[8].

$$S^{\cdot} + -CHClCH_2CHClCH_2CHClCH_2- \longrightarrow$$

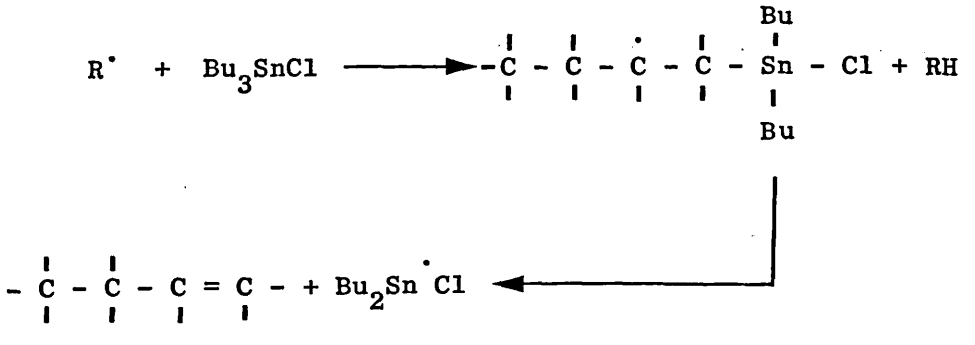
$$SH + -CHClC^{\cdot}HCHClCH_2CHClCH_2- \longrightarrow$$

$$Cl^{\cdot} + -CHClCH = CHCH_2CHClCH_2- \longrightarrow$$

$$HCl + -CHClCH = CHC^{\cdot}HCHClCH_2- \longrightarrow$$

$$Cl^{\cdot} + -CHClCH = CHCH = CHCH_2- \longrightarrow \text{ etc.}$$

If H abstraction from a butyl group takes place, as is believed to happen in the U.V. degradation of trimethyltin chloride in carbon tetrachloride (Section 2.4.1.), then the formation of double bonds becomes possible. Fish[37] reports that the most favoured position for H abstraction from an n-alkyl group is at the β carbon. Therefore



Colouration could then occur due to the formation of oligomers from the alkenes produced.

The brown viscous liquid was removed from the silica cells by pouring off the organotin solution, washing with a further amount of carbon tetrachloride, and dissolving the compound in ethanol. Evaporation of the ethanol on a watch glass produced a brown solid residue. The U.V. absorption spectrum of a solution of tributyltin chloride in carbon tetrachloride was recorded and compared to the spectrum of a similar solution that had been irradiated with U.V. light for 50 hrs., and also to a spectrum obtained from a solution of the brown solid in ethanol. (Figure XIV). These absorption spectra show that the absorption intensity of the irradiated solution is approximately 50 times that of the non-irradiated sample, is much broader, and resembles that of the brown compound. It would, therefore, appear that the coloured product formed during the irradiation was acting as a light filter with respect to the breakdown of tributyltin chloride and causing a reduction in the rate of degradation. This reduction in the breakdown rate may be seen from Figure XIII. After 50 hrs. irradiation, the breakdown of tributyltin chloride has almost ceased, although the concentration of the organotin is still quite high.

Unfortunately, the colouration of the solution meant that it would not be easy to measure the relative rates of breakdown of the butyltin chlorides. For example, the degree of colouration obtained during irradiation of a solution of dibutyltin dichloride or monobutyltin trichloride might not be as severe as observed for tributyltin chloride. Consequently the effects on the rate of breakdown might differ, and when other factors

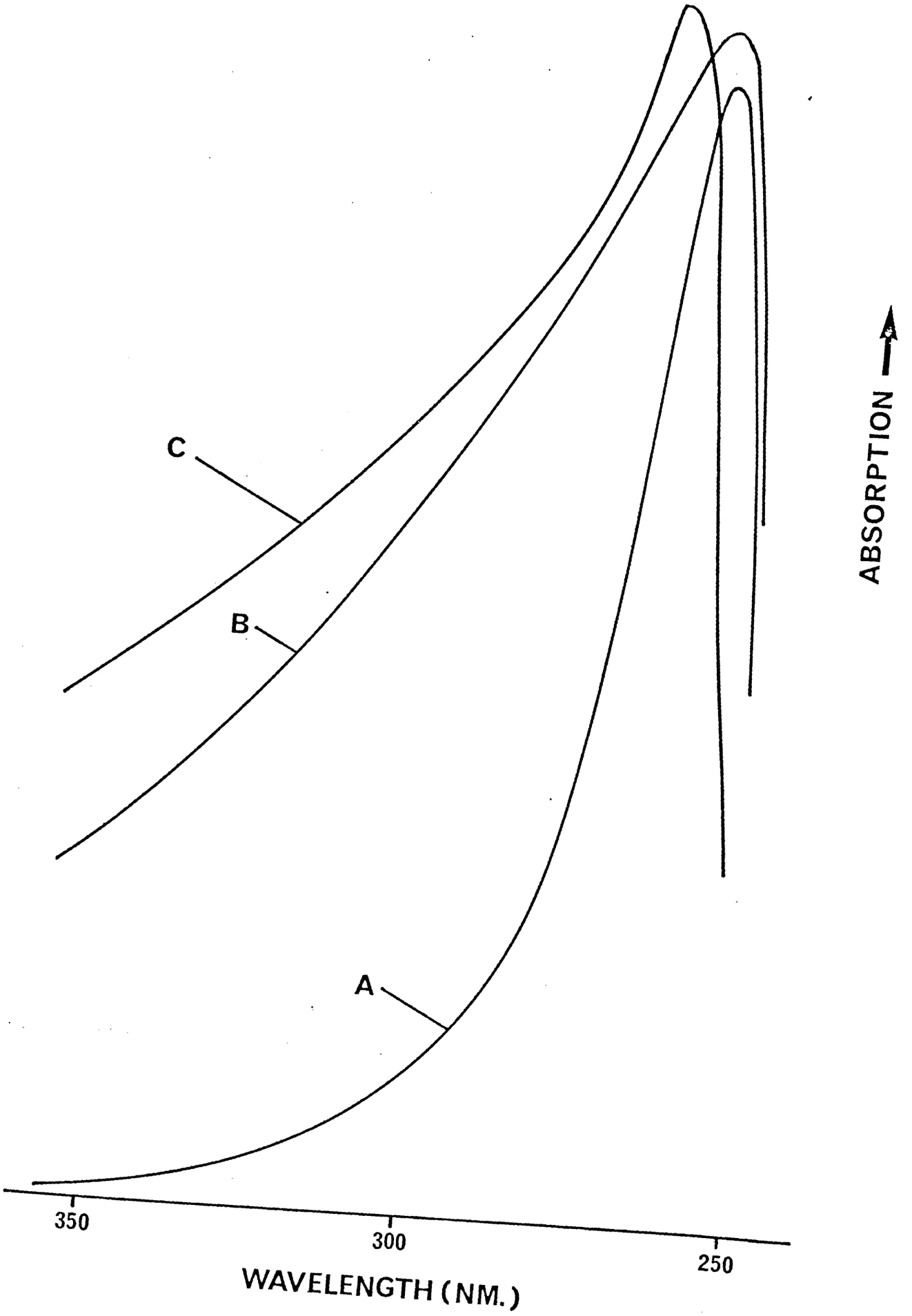
FIGURE XIV

U.V. absorption spectra of -

A) Bu_3SnCl in CCl_4 (0.15 M)

B) Solution (A) irradiated for 50 hrs. (0.003 M)

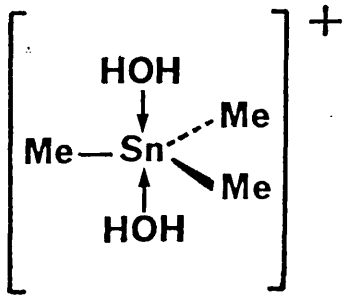
C) Residue obtained from solution (B) (11 mg/10 cm^3 ethanol).


C
B
A
ABSORPTION
350
300
250
WAVELENGTH (NM.)

such as the fluctuation in lamp emission intensity during irradiation, are considered, it can be seen that to obtain reliable figures for the breakdown rates will be difficult. Thus, the study of the degradation of the butyltin chlorides in carbon tetrachloride was not pursued further. However, the results obtained demonstrate that, upon irradiation with U.V. light, tributyltin chloride in carbon tetrachloride degrades to form dibutyltin dichloride, which is itself broken down to monobutyltin trichloride. Since dibutyltin dichloride accumulated from the breakdown of tributyltin chloride it can also be said that the rate of breakdown of tributyltin chloride is faster than that of dibutyltin dichloride.

2.4.3. U.V. degradation of trimethyltin chloride in water.

In aqueous solution, trimethyltin compounds have been shown[46] to form ionic species, although the degree of ionisation is dependent upon the pH and concentration of the solution. For example, a 10^{-3} M solution of a trimethyltin compound in water at pH less than 5 exists as the Me_3Sn^+ ion; at pH 7, the solution contains approximately 50% Me_3Sn^+ and 50% Me_3SnOH, while at pH greater than 9, the species present is almost totally Me_3SnOH[46]. The trimethyltin cation, which is predominant at low pH, has been found[47] to be hydrated and has the following structure:

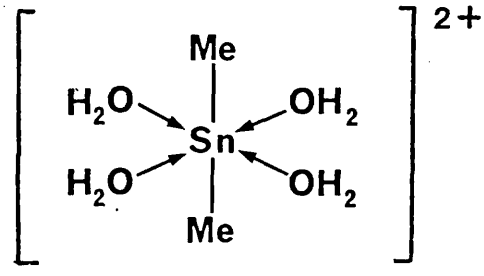


In an ^1H N.M.R. study[48] of an analogous ion, Me_3Pb^+, in aqueous solution, only one resonance was observed over the pH range 2 - 12, the chemical shift, however, changing from 1.54 - 1.26 p.p.m. relative to the methyl resonance of 2,2,dimethyl-2-silapentane-5-sulphonic acid. Therefore the equilibrium

$$Me_3Pb^+ + OH^- \rightleftharpoons Me_3PbOH$$

must be rapid compared to the N.M.R. time scale, and a similar situation might be expected for the trimethyltin ion.

Dimethyltin compounds also form ions in aqueous solution, the situation being slightly more complex, due to the formation of more species. At a concentration of 10^{-5} M at pH less than 2 the predominant dimethyltin moiety in aqueous solution is the Me_2Sn^{2+} ion; at pH 3 the solution contains approximately 50% Me_2Sn^{2+} and 50% Me_2SnOH^+ and at pH 7 the major species is $Me_2Sn(OH)_2$[46]. The dimethyltin cation, predominant at low pH, is found to be hydrated, as with the trimethyltin cation, and has the following structure[49]:



Although both the trimethyltin and dimethyltin cations have been shown to exist as hydrated species[47,49], for the purposes

of brevity they will be referred to in this text as Me_3Sn^+ and Me_2Sn^{2+} respectively.

The formation of ionic species from the introduction of monomethyltinsinto water is not observed[46]. However, Luijten[50] prepared a number of hydrolysis products of alkyltin trichlorides and found the general formula of these compounds to be

$$RSnCl_2(OH).H_2O$$

or $RSnCl(OH)_2.nH_2O$ where R = Et, n-Bu and n-Oct and n = 0 or 1.

As with the study of trimethyltin chloride in carbon tetrachoride (Section 2.4.1.), the minimum concentration of the organotin for commencing degradation was established as 0.05 M and ^1H N.M.R. spectra of trimethyltin chloride and dimethyltin dichloride in water at this concentration were recorded. Chemical shifts, δ, (upfield from the water resonance) and coupling constants, $^2J(^1H - ^{117,119}Sn)$ were measured and are given below:

	δ (p.p.m.)	$J(^1H\text{-}C\text{-}^{117}Sn)$ (Hz)	$J(^1H\text{-}C\text{-}^{119}Sn)$ (Hz)
Me_3SnCl	-4.2	65	69
Me_2SnCl_2	-3.8	102	106

A ^1H N.M.R. spectrum of a 0.05 M solution of methyltin trichloride in water showed a sharp resonance at 3.8 p.p.m. upfield from water and a broad resonance centered 4.0 p.p.m. upfield from water. This effect will be discussed in Section 2.6. However, as a practical consequence, the coincidence of

one of these peaks with the dimethyltin resonance meant that it would be very difficult to detect small amounts of aqueous monomethyltin trichloride in the presence of a dimethyltin species. Also, since more than one reasonance was present the signal-to-noise ratio was correspondingly decreased and so quantitative measurements of aqueous solutions of monomethyltin trichloride at this concentration were not possible.

Redistribution reactions of the methyltin chlorides in water were investigated by preparing mixtures of the compounds and periodically obtaining a ^1H N.M.R. spectrum, as with the carbon tetrachloride system, but no reactions were seen to be occurring.

U.V. absorption spectra of the methyltin chlorides 0.05 M in water, are shown in Figure XV. Trimethyltin chloride gave a single absorption with a maximum at 208 nm., dimethyltin dichloride gave two peaks with maxima at 203 nm and 228 nm., and methyltin trichloride gave a single broad peak, with a maximum at 220 nm. The pH of these solutions were 3.6, 2.4 and 1.4 respectively. At a pH of less than 5, trimethyltins have been said to exist as the hydrated Me_3Sn^+ ion. The dimethyltin solution, however, at a pH of 2.4 will contain a mixture of hydrated Me_2Sn^{2+} and $Me_2Sn(OH)^+$, possibly explaining the observation of 2 peaks in the U.V. absorption spectrum. The fact that only one resonance is observed in the ^1H N.M.R. spectrum is not unexpected, since this indicates that any equilibrium existing between the two species is rapid on the N.M.R. time scale but slow compared to electronic transitions. The broadness of the spectrum given by methyltin trichloride might be due to the presence of more than one species, as indicated by the ^1H N.M.R. spectrum.

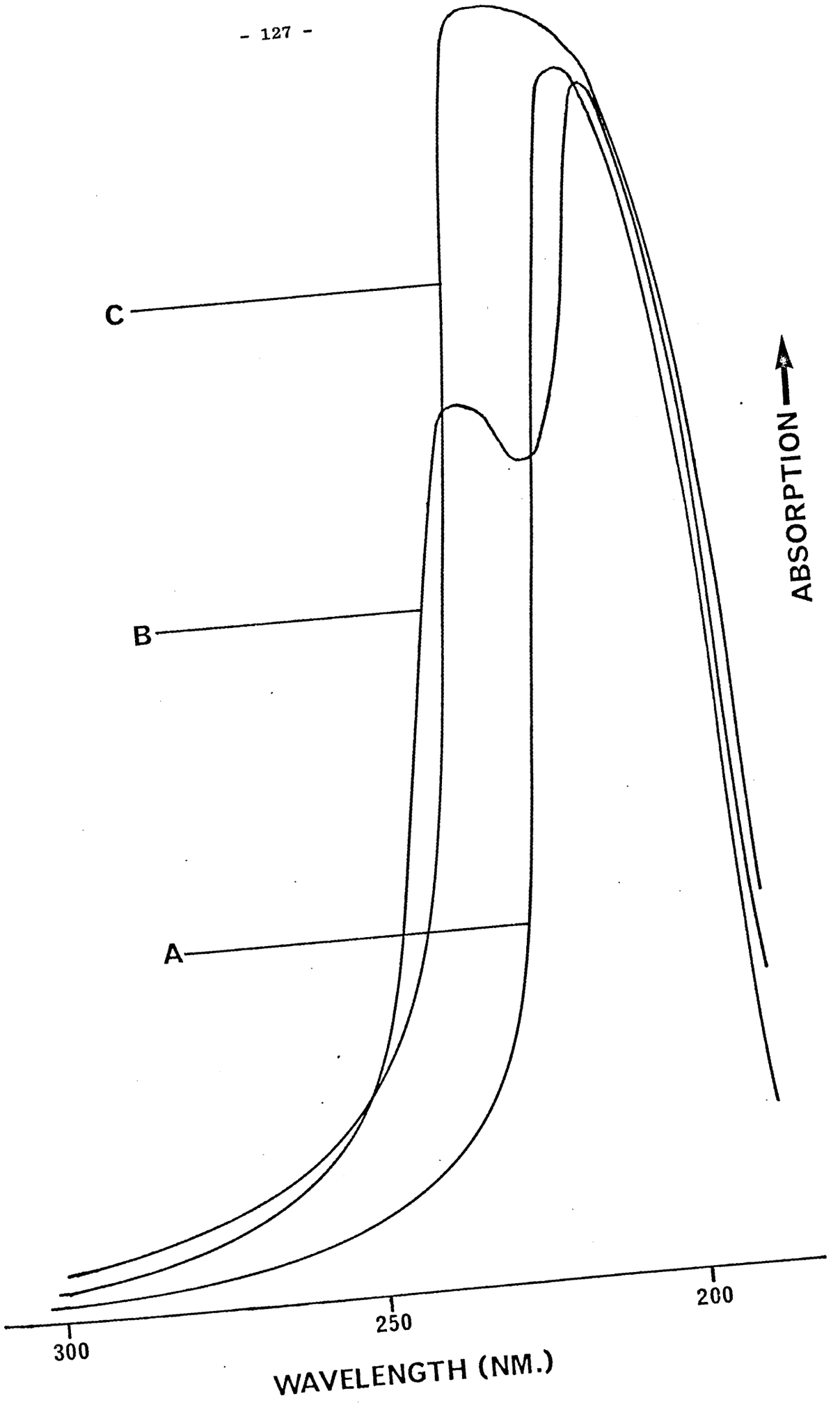
FIGURE XV

U.V. absorption spectra of Me_nSnCl_{4-n} (0.05 M in H_2O)

A) Me_3SnCl - λ (ABS. MAX) = 208 nm.

B) Me_2SnCl_2 - " " " = 203 nm and 227 nm.

C) $MeSnCl_3$ - " " " = 220 nm.


C
B
A
ABSORPTION
300
250
200
WAVELENGTH (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 system, would result in a much slower rate of breakdown. Water does not absorb light of wavelengths of 200 nm. or above, and therefore it is possible to irradiate samples with light of such wavelengths, without fear of U.V. induced homolytic bond cleavage of the solvent affecting the rate of breakdown of the organotin compound.

Thus, solutions of 0.05 M trimethyltin chloride in water were irradiated for increasing periods of time with U.V. light of wavelengths upwards of 200 nm. The intensity of irradiation at the sample position was as follows: 200-300 nm $\simeq$ 2 mwatts cm^{-2}; 300-400 nm $\approx$ 8 mwatts cm^{-2}. A problem occurred during irradiation, due to the formation of a fine suspended white precipitate which acted as a light filter and prevented further degradation. Therefore, solutions had to be periodically centrifuged in order to remove this fine precipitate. ^{1}H N.M.R. spectra of the irradiated solutions showed a peak due to the trimethyltin compound and a second peak 0.4 p.p.m. downfield of this, which, after reaching sufficient intensity, was identified from the magnitude of the proton-tin coupling as being due to a dimethyltin species. From the work of Tobias[46] this will be assumed to be the dimethyltin cation. Quantitative measurements of the concentrations of tri- and di-methyltin species with respect to irradiation time are given in Table VII.

No features were seen on any of the N.M.R. spectra of the degraded trimethyltin solutions which could be attributed

TABLE VII: Results of the U.V. degradation of the trimethyltin cation, 0.05 M in water.

t (hrs.)	N	Trimethyltin $\overline{A}$ (M)	Trimethyltin σ_{N-1}	Dimethyltin $\overline{A}$ (M)	Dimethyltin σ_{N-1}
0		0.05	-	0.00	-
5	6	0.046	0.002	0.003	0.001
10	5	0.040	0.003	0.004	0.001
15	5	0.033	0.002	0.005	0.001
20	5	0.031	0.002	0.006	0.001
35	4	0.021	0.001	0.012	0.003
45	2	0.018	0.001	0.016	0.001
65	5	0.010	0.001	0.017	0.001
80	4	0.007	0.001	0.018	0.001
90	5	0.005	0.001	0.018	0.001
110	3	0.003	0.001	0.017	0.001
120	3	0.003	0.001	0.016	0.001

t = irradiation time

N = number of samples

$\overline{A}$ = mean concentration

σ_{N-1} = standard deviation of $\overline{A}$ for N-1 samples

to the presence of a monomethyltin compound. However, due to the difficulties in detecting such species by ^{1}H N.M.R. spectroscopy some solutions were qualitatively investigated by paper-chromatography[39] and, although, this revealed the presence of dimethyltin and inorganic tin as degradation products, still no monomethyltin was found.

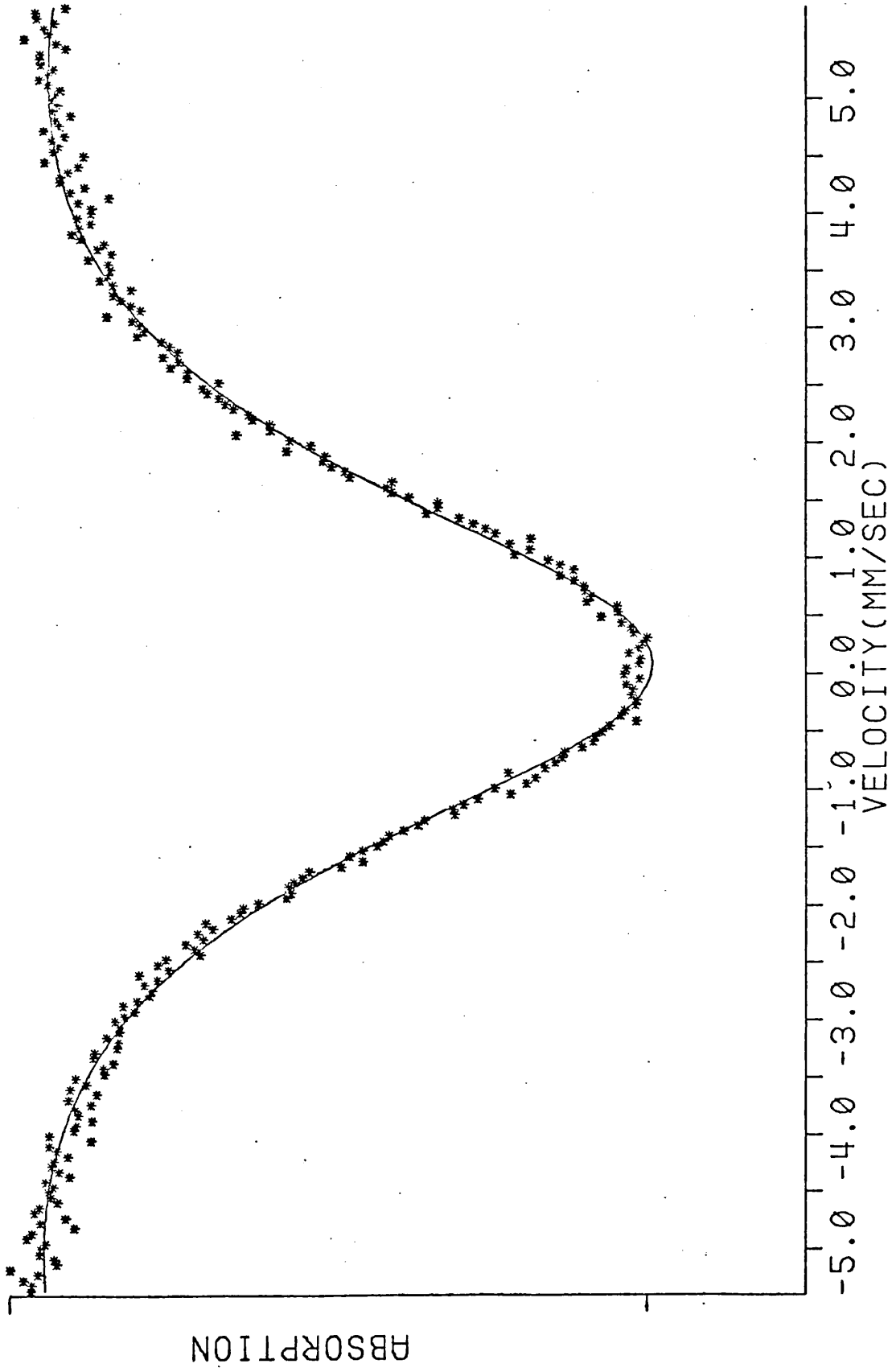
In a study of the U.V. degradation of triphenyltin hydroxide in water at concentrations of approximately 1 p.p.m. and 6 p.p.m., Soderquist and Crosby[19] determined diphenyltin and inorganic tin as degradation products but did not detect any monophenyltin species. The method of analysis employed for this study was extraction from water, followed by conversion to the organotin hydride and determination by electron capture gas-liquid chromatography[51]. It was concluded that the failure to detect any monophenyltin was due to the formation of a polymeric monophenyltin species of the type $(PhSnO_xH_y)_z$ which was water soluble and consequently non-extractable. A similar argument cannot, however, explain the failure to detect a monomethyltin species in the present investigation. Such a polymeric species would have been detected by the paper-chromatographic separation of the irradiated solutions. Therefore, it is believed that no monomethyltin species accumulates from the U.V. degradation of trimethyltin chloride in water.

Analysis of the white precipitate centrifuged from the irradiated solutions and a subsequent ^{119m}Sn Mössbauer spectrum (Figure XVI) revealed that the compound was a hydrated form of SnO_2. The amount of this compound was not measured quantitatively after each irradiation, but, allowing for a slight loss of volume for each centrifugation, the total weight of hydrated SnO_2 produced after 110 hours irradiation was, within experimental error, that

FIGURE XVI

^{119m}Sn Mössbauer spectrum of the white precipitate formed in the U.V. degradation of the trimethyltin cation in water, showing it to be stannic oxide:

	δ = 0.05 mm.sec^{-1}	ΔE_Q = 0.00 mm.sec^{-1}
Lit.[52]	δ = 0.00 mm sec^{-1}	ΔE_Q = 0.00 mm.sec^{-1}


ABSORPTION
-5.0 -4.0 -3.0 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 5.0
VELOCITY(MM/SEC)

which would account for the difference between the starting concentration and the total organotin concentration, i.e. tri- and di-methyltin. Therefore, the molarity of SnO_2 produced after t hour's irradiation may be found from:

Molarity SnO_2 = total molarity - total organotin molarity at time, t.

Values for the concentration of inorganic tin with respect to irradiation time are given in Table VIII, and Figure XVII shows a graph of Tables VII and VIII representing the U.V. degradation of a 0.05 M solution of the trimethyltin cation in water.

A plot of ln (A_o/A) vs t for the results of the breakdown of the trimethyltin species gave a straight line, revealing that the compound was degrading exponentially, under measured irradiation conditions, with a half-life of approximately 30 hrs.

In order to establish the relative rates of breakdown of the methyltin chlorides in aqueous solution, two samples each of trimethyltin chloride, dimethyltin dichloride and monomethyltin trichloride, 0.05 M in water, were irradiated simultaneously, so as to avoid differences due to fluctuation in the lamp emission. The intensity of irradiation was measured to be: 200-300 nm. $\simeq$ 1 mwatt cm^{-2}; 300-400 nm. $\simeq$ 6 mwatts cm^{-2}. At this irradiation intensity, the trimethyltin solution was found to break down with a half-life of approximately 60 hrs. The dimethyltin dichloride solution degraded forming a precipitate of hydrated SnO_2, but, once again, no monomethyltin species were detected in the irradiated solutions. The rate of degradation was slower than that of the trimethyltin solution, and approximately 20% of the compound had broken down after 110 hours or irradiation. Since accurate measurement of the rate of break-

TABLE VIII: The concentration of stannic oxide produced with respect to the irradiation time of a 0.05 M aqueous solution of the trimethyltin cation.

Irradiation time (hrs.)	Concentration of SnO_2 (M)
0	0.0
5	0.001
10	0.004
15	0.008
20	0.011
35	0.017
45	0.016
65	0.023
80	0.025
90	0.027
110	0.030
120	0.031

FIGURE XVII

The U.V. degradation of the trimethyltin cation, Me_3Sn^+, 0.05 M in water.

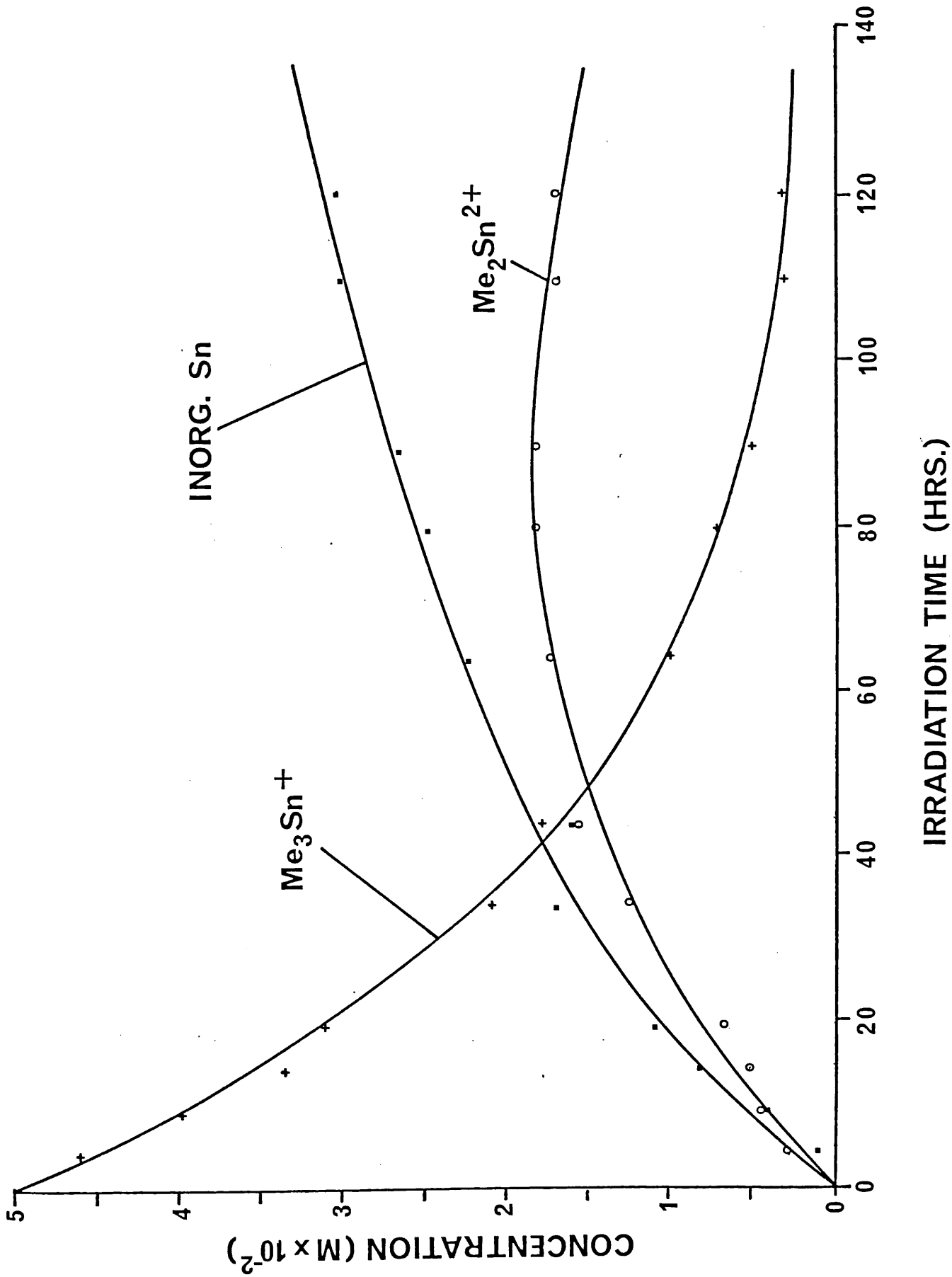
Irradiation intensities 200-300 nm. ≈ 2 mwatts cm^{-2}

300-400 nm. ≈ 8 mwatts cm^{-2}

+ - Me_3Sn^+

0 - Me_2Sn^{2+}

▪ - Inorg Sn


INORG. Sn
Me_2Sn^{2+}
Me_3Sn^+
CONCENTRATION ($M \times 10^{-2}$)
IRRADIATION TIME (HRS.)
0
1
2
3
4
5
0
20
40
60
80
100
120
140

down of dimethyltin dichloride in water would have involved long irradiation times, the half-life was estimated (after 110 hours of irradiation) to have been approximately 300 hours, 5 times slower than that of the trimethyltin species. Monomethyltin trichloride in water was found to degrade at a much slower rate and, thus, measurement of the half-life was not possible. However, the formation of a visible precipitate of hydrated SnO_2 was noticed after approximately 30 hours of irradiation. With the dimethyltin solution the precipitate first appeared after about 6 hours irradiation. Therefore, as a very rough estimate it may be said that the rate of breakdown of the monomethyltin species is at least 5 times slower than that of the dimethyltin derivatives.

The presence of dissolved oxygen in the degradation solutions in no way affected either the products formed or the rates of reaction, since identical results were obtained for the breakdown of the tri-, di- and mono-methyltin compounds whether the samples were irradiated under an atmosphere of argon, in solutions which had been degassed or open to the air.

From the results obtained for the degradation procedure, it might be thought that the reaction was simply:

$$Me_3Sn^+ \longrightarrow Me_2Sn^{2+} \longrightarrow SnO_2$$

However, it is impossible for the above reaction sequence to generate results such as are shown in Figure XVII. The concentration of the dimethyltin species is far too low in the initial stages of the procedure for such a reaction sequence and the concentration of inorganic tin is correspondingly too high. These results representing the initial stages of the

reaction were verified by irradiation of more samples, but the same pattern was still obtained.

To check that the equilibrium existing between the two dimethyltin species, Me_2Sn^{2+} and $Me_2Sn(OH)^{+}$, in solution, was not affecting the intensity of the N.M.R. signal, solutions of 0.05 M dimethyltin dichloride in water were prepared over a pH range 2-4 and ^1H N.M.R. spectra recorded. However, the pH, and consequently the ratio of the two species, did not affect the N.M.R. intensity, so the measured concentrations of dimethyltin species were taken as being correct. Thus, the degradation procedure appears to be more complex than may be represented by a simple series reaction. However, it will now be shown that a modification of this simple first order picture provides a useful explanation of the experimental observations.

A plot of ln (A_o/A) vs t, for the breakdown of the trimethyltin cation gave a straight line, revealing that the results very closely follow an exponential line, and the rate constant, K_1, was found to equal 0.025 $hr.^{-1}$. From the simultaneous irradiation of aqueous solutions of trimethyltin chloride and dimethyltin dichloride, it was known that the rate of breakdown of the latter was approximately five times slower than that of the former. Therefore, the rate constant, K_2, representing the breakdown of the dimethyltin species is given by:

$$K_2 = K_1/5 = 0.005 \text{ hr}^{-1}$$

Concentrations with respect to time, for a series first-

order reaction of the type

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

may be calculated from the expressions given in Section 2.4.1. A graph representing a theoretical series first-order reaction, where K_1 and K_2 have the above mentioned values is therefore shown in Figure XVIII. It can be seen that the maximum concentration of B occurs at approximately 80 hours, and this corresponds to the time of maximum concentration of the dimethyltin species obtained from experimental results (see Figure XVII), perhaps giving further evidence that the relative rates of breakdown of the two species are correct. The shape of the theoretical graph (Figure XVIII) may be modified by assuming that not all of species A degrades forming B, but that a certain percentage forms another species B'

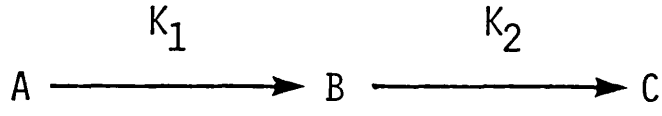
<u>i.e.</u> A ⟶ X% B

A ⟶ Y% B'

If B' also breaks down forming C, with a rate which is fast compared to its formation from A, then its concentration may be neglected, and the concentration of C at any given time is found to be higher than would be observed had the reaction proceeded along only one route. In fact, if the relative rates of breakdown are taken as before, but it is assumed that only approximately 55% of A forms B, theoretical concentrations may be calculated (Figure XIX) which reproduce the experimental results rather well. Thus, with regard to the degradation of

FIGURE XVIII

A theoretical series first-order reaction of the type



$K_1 = 0.025\ hr.^{-1}$ $K_2 = 0.005\ hr^{-1}$

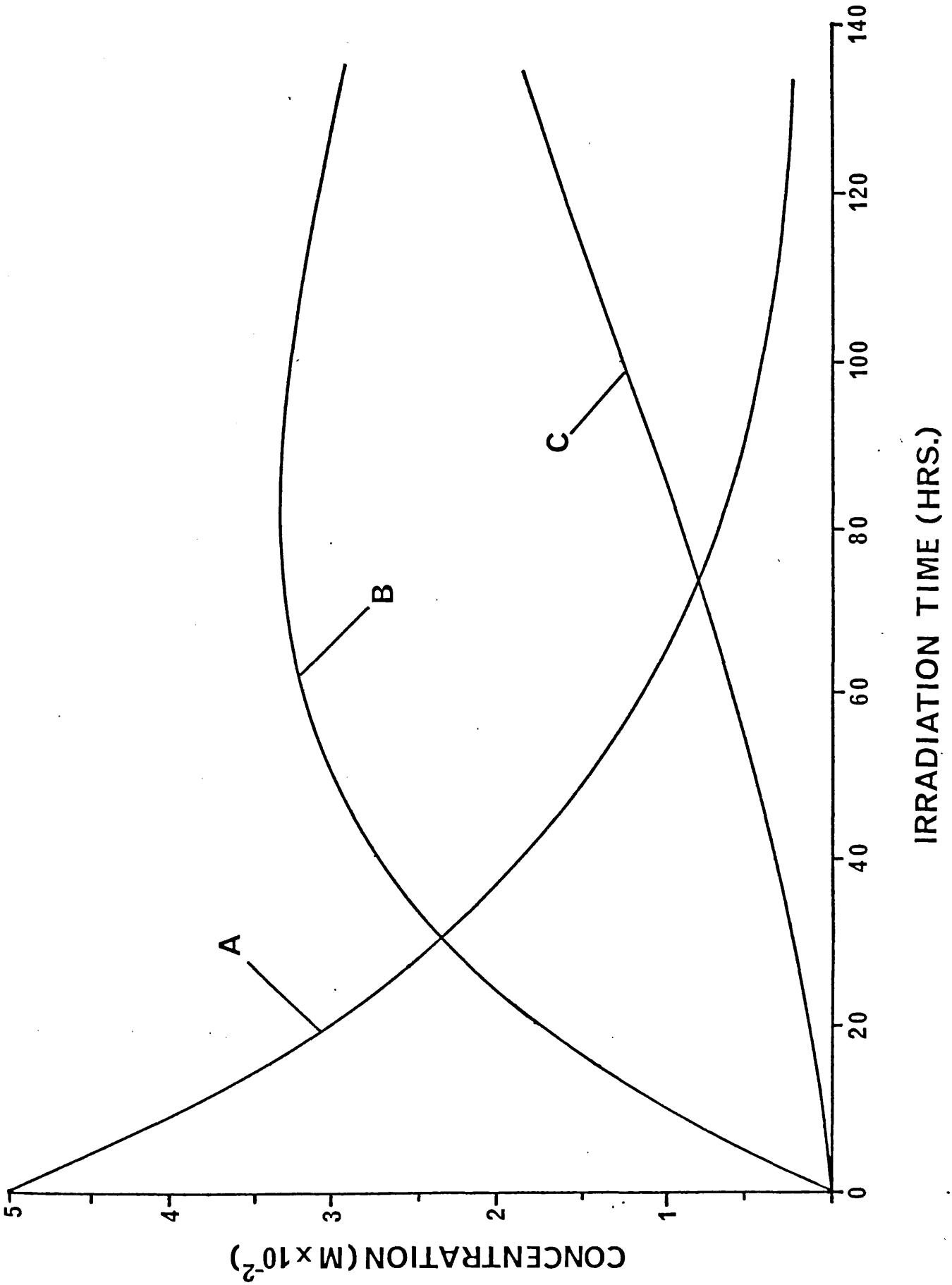
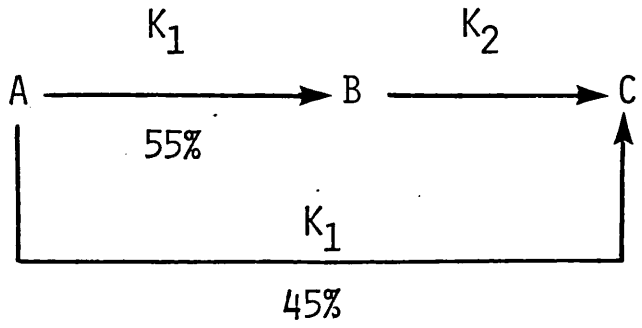

CONCENTRATION (M x 10⁻²)
5
4
3
2
1
0
20
40
60
80
100
120
140
IRRADIATION TIME (HRS.)
A
B
C

FIGURE XIX

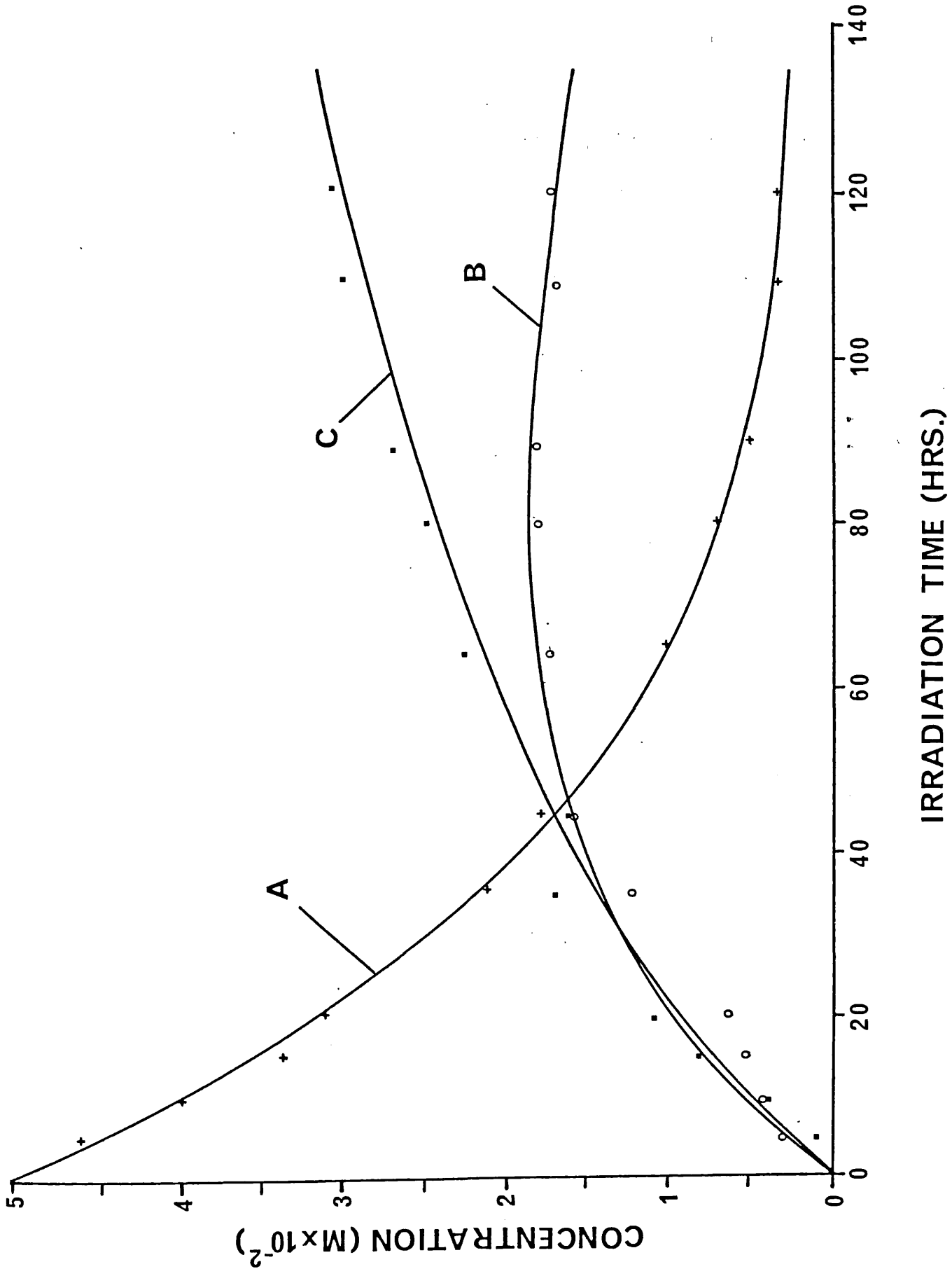
A theorectical series first order reaction of the type



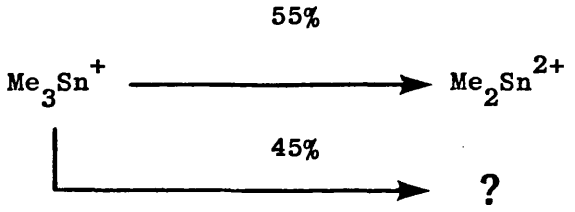
$K_1 = 0.025 \ hr^{-1}$ $K_2 = 0.005 \ hr^{-1}$

N.B. Experimental results from Tables VII and VIII are included for comparison

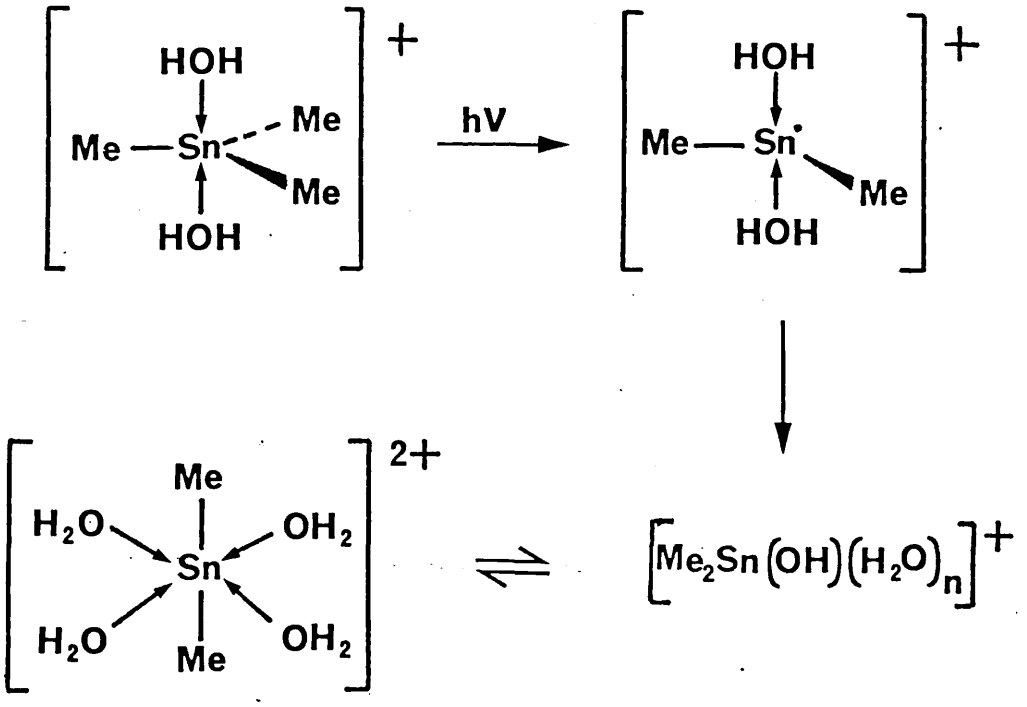
+ - Me_3Sn^+
0 - Me_2Sn^{2+}
■ - Inorg. Sn.


A
B
C
CONCENTRATION (M x 10⁻²)
IRRADIATION TIME (HRS.)
0
1
2
3
4
5
0
20
40
60
80
100
120
140

the trimethyltin cation, we have:



Very little is known about the reactions of organotin free radicals in aqueous solution, but if it is assumed that cleavage of a Sn-C bond by U.V. light produces an organotin radical, it is likely that it would react with a water molecule, possibly even with one of the coordinated water molecules. It is known[46] that the detected dimethyltin cation, Me_2Sn^{2+} is in equilibrium in aqueous solution with the species, $Me_2Sn(OH)^+$. Therefore, reaction of an organotin radical in water probably leads to the formation of a Sn-OH bond.



The remaining problem is to understand what happens to the 45% of the trimethyltin cation that does not appear to be converted to the dimethyltin ion. Christianson *et al*[53] in a flash photolysis study of tetraethyltin and tetravinyltin found that absorption of light of wavelengths between 190-240 nm. by the organotins led to the simultaneous cleavage of two Sn-C bonds. The maximum absorption wavelength of the trimethyltin cation is at 210 nm (136 kcals mol^{-1}) and since the bond dissociation energy for a Sn-Me bond is only approximately 52 kcals mol^{-1},[22] there is sufficient energy available for a similar process to be occurring to some of the trimethyltin cation, *i.e.* more than one Sn-Me bond may be broken by the absorption of light. The most likely process, therefore, is that whereby two Sn-Me bonds are broken, leading to the formation of a monomethyltin species. However, since no monomethyltin compounds were 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 known from the available information, but it can be said that the species is not that which is formed upon dissolution of methyltin trichloride in water, this was shown to have a very slow breakdown. Cleavage of the two Sn-C bonds would presumably result in the formation of a monomethyltin diradical

$$(Me_3Sn)^+ \xrightarrow{h\nu} (MeSn^{\cdot\cdot})^+$$

If the spins of the two free electrons become paired this would result in the formation of a tin(II) compound, but it is unlikely that the species exists long enough for this to occur. The

most likely process to occur, therefore, is that of reaction with the solvent.

In the same way that two Sn-Me bonds seem to be broken for a percentage of trimethyltin cation, so too could a similar situation be occurring with the degradation of the dimethyltin cation. In this case, however, the failure to detect monomethyltin prevents any estimation as to the percentage that is breaking down by each mechanism.

The end product resulting from the reaction of organotin radicals with water is expected to be $Sn(OH)_4$. Such a species would exist, in aqueous solution, in an equilibrium as shown below:

$$Sn^{4+} \rightleftharpoons Sn(OH)^{3+} \rightleftharpoons Sn(OH)_2^{2+} \rightleftharpoons Sn(OH)_3^{+} \rightleftharpoons Sn(OH)_4$$

increasing pH $\longrightarrow$

The hydrated Sn^{4+} ion is only present in solution at a pH of less than 1,[54] and at the pH of the irradiated solutions, (pH 2-3), $Sn(OH)_4$ should be present[54]. There is, however, no direct evidence for the existence of $Sn(OH)_4$[55], and it is in fact found that such a species precipitates as a hydrated form of tin(IV) oxide - the detected end product of the degradation reaction.

Attempts at identifying the non-tin containing products of the degradation reactions by irradiating samples in sealed tubes and then recording the ^1H N.M.R. spectra were unsuccessful, due to the formation of the tin oxide precipitate, which would not remain on the bottom of the N.M.R. tube whilst spinning the sample in the spectrometer. The consequent inhomogeneity of

the sample resulted in broadened resonances and, thus, a reduction in the signal-to-noise ratio. Spectra recorded from samples which had been irradiated in unsealed tubes and which had been centrifuged to remove the precipitate only revealed a small amount of methanol, presumably formed from

$$Me^{\cdot} + H_2O \longrightarrow MeOH + H^{\cdot}$$

The concentration of methanol detected was far too low to account for all the methyl groups that would have been produced by the organotin degradation. Therefore the major non-tin containing products are likely to be gaseous e.g. methane and ethane, and these were not detected, due to their aqueous solubility being below the limit of detection of the N.M.R. instrument. If methane is produced, it is probably formed by the reaction of a methyl radical with the solvent rather than by H abstraction from an organotin molecule, as was found to be occurring in the degradation of trimethyltin chloride in carbon tetrachloride (Section 2.4.1.). The presence of significant H abstraction would not be consistent with the observed exponential breakdown curve. The formation of ethane could arise from the combination of two methyl radicals. In order for the complete reaction mechanism of the degradation of the trimethyltin cation in water to be established, the non-tin containing products would need to be positively identified. Since this was not possibly by ^1H N.M.R. spectroscopy an investigation would need to be carried out on the gases evolved during the degradation by an alternate analytical technique, e.g. gas chromatography.

The results discussed so far were all obtained by irradiating the samples with light of wavelengths greater than 200 nm. In

the environment, irradiation would occur from the sun, but sunlight at sea-level does not contain much light below 290 nm.[56] Light of wavelength of 300 nm. possesses an energy of 96 kcals. mol^{-1}, which is still sufficient to break a Sn-C bond, providing it is absorbed. Therefore, in order to demonstrate that breakdown would still occur by irradiation with higher wavelengths, a sample of 0.05 M trimethyltin chloride in water was irradiated behind a glass plate which cut out all light of wavelength less than 300 nm. After 250 hrs. irradiation, a ^{1}H N.M.R. spectrum was recorded. This revealed that the trimethyltin concentration had decreased to approximately 0.046 M and the presence of a dimethyltin species in solution was detected. By comparison of this result with Figure XVII it was estimated that the half-life for the breakdown would have been between 1100-1300 hrs. Some of this large increase in the half-life can be ascribed to the reduction in the overall light intensity, caused by cutting out light below 300 nm. but the main cause must be the weak absorption, by the organotins in aqueous solution, of light of these higher wavelengths. However, the important fact was that degradation was still occurring.

2.5. The nature of tributyltin compounds in aqueous solution.

The study of an aqueous organotin degradation (Section 2.4.3.) was carried out using trimethyltin chloride, since this compound has a sufficiently high solubility to permit simple analysis. But, as mentioned previously, it is the tributyl- and triphenyl-tin compounds that have commercial applications, although their aqueous solubility is usually only in the order of a few p.p.m., *e.g.* solubility of bis(tri-*n*-butyltin) oxide in sea water = 1.4 p.p.m.;[57] aqueous solubility of triphenyltin

acetate at pH 8.0 = 2.9 p.p.m.[58]. However, a group of tributyltin compounds that have been shown[59] to possess a much higher aqueous solubility are the tributyltin alkanesulphonates, Bu_3SnO_3SR.

Saturated solutions of a series of these compounds were prepared by shaking the tributyltin compound with distilled water for 30 mins., at 25^{0}C and then leaving to stand overnight, to allow undissolved matter to settle. Solutions were filtered, if necessary, and suitable aliquots subsequently taken after 1 day, 1 month and 2 months, the samples being stored in the dark. The amount of the compounds retained in solutions was determined by wet ashing the aliquot sample with nitric/sulphuric acids and determining the total tin content by iodimetric titration. The water solubilities of the tributyltin alkane- and arene-sulphonates studied, together with two triphenyltin analogues for comparison, are therefore given in Table IX. These results show that the aqueous solubilities for the tributyltin alkanesulphonates (approximately 5000-20,000 p.p.m.) are remarkably high for tributyltin compounds, and are in the range required for most biocidal applications.

^{119}Sn F.T.N.M.R. spectra were recorded for a saturated aqueous solution of the most soluble compound, tributyltin ethanesulphonate, and also for a 10% w/v aqueous solution of trimethyltin chloride, the ^{119}Sn chemical shifts are given in Table X.

It can be seen that the chemical shift value recorded for the aqueous solution of tributyltin ethanesulphonate is approximately 20 p.p.m. to high field of that of trimethyltin chloride in water. A shift of 20 p.p.m. to high field is often found to occur upon

Table IX: Water solubilities of R_3SnO_3SR' compounds at 25°C

Compound	Solubility of compound, w/v%, ± 0.1) After 1 day	1 month	2 months
Bu_3SnO_3SPh	0.2	0.5	0.6
$Bu_3SnO_3SC_6H_4Me$-4	0.4	0.4	a
$Bu_3SnO_3SC_6H_3Cl$-4, NH_2-5	0.06	a	a
$Bu_3SnO_3SCF_3$	0.1	0.7	0.8
Bu_3SnO_3SMe	1.1[b]	> 1.6[c]	a
Bu_3SnO_3SEt	1.5[b]	1.9	1.9
$Bu_3SnO_3S^nBu$	0.8	0.8	0.8
$Bu_3SnO_3S^tBu$	0.7	0.8	0.8
$Bu_3SnO_3SNH_3$	0.6[d]	1.3	1.6
$Bu_3SnO_3SN(SnBu_3)_2$	0.05	0.3	0.6
Ph_3SnO_3SPh	0.07	a	a
Ph_3SnO_3SEt	0.13	a	a

[a] Analysis not performed

[b] Ref.60 reports 3-10%

[c] The initial solution was a nominal 1.5%

[d] Ref.61 reports 22%.

Table X: ^{119}Sn chemical shifts, $\delta\ ^{119}Sn$.[a]

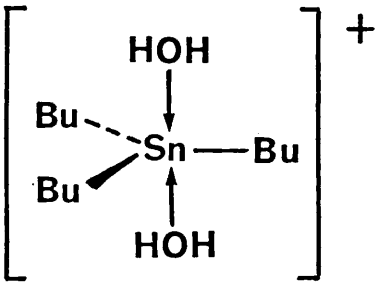
Compound	Solvent	$\delta\ ^{119}Sn$ (p.p.m.)
Bu_3SnO_3SEt	H_2O	21.5
Me_3SnCl	H_2O	40.1
Me_3SnCl	CCl_4	164[b]
$Me_2BuSnCl$	Neat Liquid	157.1[b]
Bu_3SnCl	CCl_4	141[b]

[a] Relative to Me_4Sn

[b] From reference 44.

substitution of the methyl groups in a trimethyltin species by n-butyl radicals. This is due to the greater electron releasing power of the butyl group increasing the shielding. The ^{119}Sn chemical shifts of Me_3SnCl, $Me_2BuSnCl$ and Bu_3SnCl are included in Table X for comparison. Therefore, since it is known[47] that trimethyltin chloride in water forms the hydrated trimethyltin cation, $\{Me_3Sn(H_2O)_2\}^+$, it is proposed that the species present in an aqueous solution of tributyltin ethanesulphonate is the hydrated tributyltin cation

i.e.



The ^{119m}Sn Mössbauer parameters of some tributyl- and triphenyltin sulphonates are given in Table XI. The large quadrupole splittings, ΔE_Q, (3.90 - 4.46 mm. sec^{-1}) are indicative[63] of an infinite chain polymeric structure in the solid state, in which the sulphonate groups bridge planar R_3Sn moieties.

i.e.

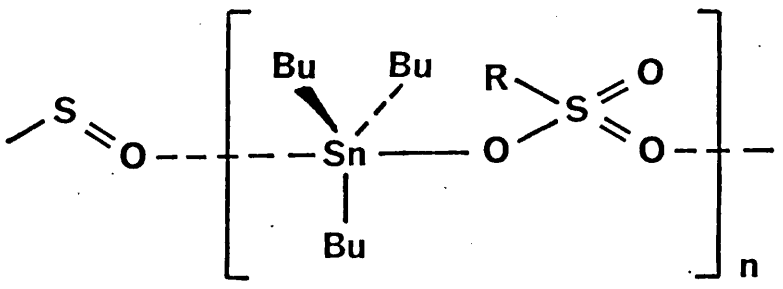


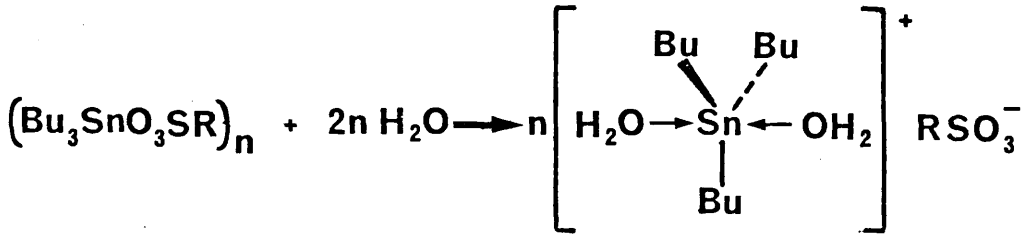
Table XI: ^{119m}Sn Mössbauer parameters for R_3SnO_3SR' compounds

Compound	δ (mm sec^{-1})	ΔE_Q (mm sec^{-1})
Bu_3SnO_3SMe	1.59	4.36
Bu_3SnO_3SEt	1.5[a]	4.31[a]
$Bu_3SnO_3SC_6H_4Me$-4	1.56	4.46
Ph_3SnO_3SEt	1.36	3.98
Ph_3SnO_3SPh	1.38[b]	3.90[b]

[a] Ref. 62

[b] Ref. 63

It was found that the solubilities of most of the compounds increased on standing for a period of time and this was probably due to the ease with which the water molecules were able to break up the self-associated polymeric structure.



The pH values of saturated solutions of the tributyltin alkanesulphonates were recorded and found to be in the range 2.5 - 2.8. The fairly acidic solutions provide further evidence for the formation of the hydrated tributyltin cation, because previous observations[47] of similar pH values for aqueous solutions of trialkyltin salts (e.g. Me_3SnBr) were ascribed to the partial dissociation of the hydrated trialkyltin cation

i.e. $\{R_3Sn(H_2O)_2\}^+X^- \rightarrow R_3SnOH + HX + H_2O.$

The U.V. absorption spectrum of the aqueous tributyltin ethanesulphonate solution was recorded and it was found that the maximum absorption wavelength was at 210 nm. This corresponds to the absorption wavelength of the hydrated trimethyltin cation, but the absorption intensity of the tributyltin analogue was approximately 10 times as great. A qualitative investigation by paper chromatography on the

stability of the compound in solution did not show the presence of any dibutyltin species after 2-3 months of standing in normal daylight. However, this does not necessarily mean that no breakdown had occurred, for it is possible that the insoluble dibutyltin oxide had been produced, which would not be detected in solution. Irradiation of the tributyltin ethanesulphonate solution in silica cells with U.V. light of wavelengths greater than 200 nm., produced a dense white precipitate. A paper - chromatographic investigation[39] of the irradiated solution revealed the presence of a dibutyltin species, which was present either in solution or as a suspension. Thus, breakdown was occurring. The rate of breakdown was not measured, but it appeared to be faster than that of the trimethyltin cation (Section 2.4.1.). This is probably due to the intensity of absorption being greater for the tributyltin species and also because the Sn-Bu bond is weaker than the Sn-Me bond (Section 1.2.). The white precipitate produced during irradiation was not identified, but it is believed, from a chromatographic investigation[39], that the compound was not a tin-containing species.

2.6. Spectroscopic investigation of the hydrolysis products of monoalkyltin trichlorides.

In Section 2.4.3. it was noted that a ^{1}H N.M.R. spectrum of a 0.05 M aqueous solution of methyltin trichloride indicated the presence of more than one species. This effect has been reported previously by Van den Berghe and Van der Kelen[64], who recorded 60 MHz ^{1}H N.M.R. spectra of methyltin trichloride in water and found that, at concentrations above 0.21 M, only one peak was present, whereas at lower concentrations a second broad resonance

appeared upfield from the main signal. This effect may be seen in Figure XX which shows 90 MHz ^{1}H N.M.R. spectra of methyltin trichloride in water at concentrations of (a) 0.5 M, (b) 0.25 M and (c) 0.05 M. The spectrum of the 0.05 M solution (Figure XX (c)) shows a shoulder on the broad resonance, which was not observed by previous workers[64], indicating the possibility of three species in solution, and this is clearly demonstrated by a 400 MHz ^{1}H N.M.R. spectrum of the same solution (Figure XXI). It can be seen that $^{117,119}Sn$ satellites are associated with each of the three peaks, revealing that they are due to organotin species. The broadness of both the central and satellite features probably indicates chemical exchange between these species. ^{1}H chemical shifts, $\delta\ ^{1}H$, (relative to the water resonance) and coupling constants, $^{2}J(^{117,119}Sn - ^{1}H)$, for the peaks shown in Figures XX and XXI are given in Table XII.

^{119}Sn N.M.R. spectra of the 0.5 M and 0.25 M solutions gave just one peak at -481 and -486 p.p.m. respectively, while the 0.05 M solution showed two peaks at -498 and -515 p.p.m.. From the ^{1}H spectrum of the 0.05 M solution (Figure XXI) three peaks were expected in the ^{119}Sn spectrum. It is possible, however, that the signal from a third species was not detectable above the noise level in the spectrum.

A series of first hydrolysis products of monoalkyltin trichlorides have been prepared, by Luijten[50], by hydrolysis in moist air. The general formula of these species was found[50] to be $RSnCl_2(OH).H_2O$, where R = Et, Bu or Oct, and the structure of the ethyl derivative

FIGURE XX

90 MHz ^{1}H N.M.R. SPECTRA OF AQUEOUS SOLUTIONS OF METHYLTIN TRICHLORIDE.

(a) 0.5 M

(b) 0.25 M

(c) 0.05 M

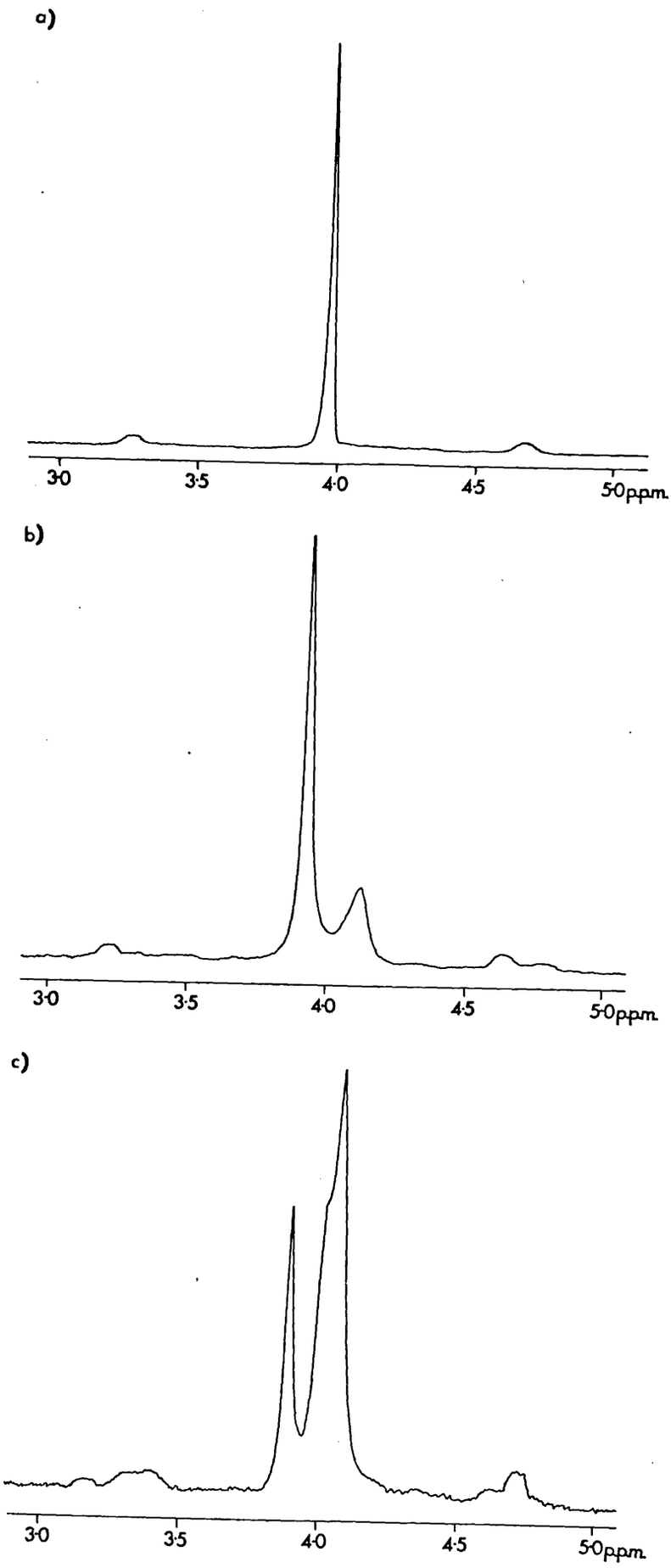

a)
3·0
3·5
4·0
4·5
5·0ppm.
b)
3·0
3·5
4·0
4·5
5·0ppm.
c)
3·0
3·5
4·0
4·5
5·0ppm.

FIGURE XXI

400 MHz ^{1}H N.M.R. SPECTRUM OF A 0.05 M AQUEOUS SOLUTION OF METHYLTIN TRICHLORIDE.

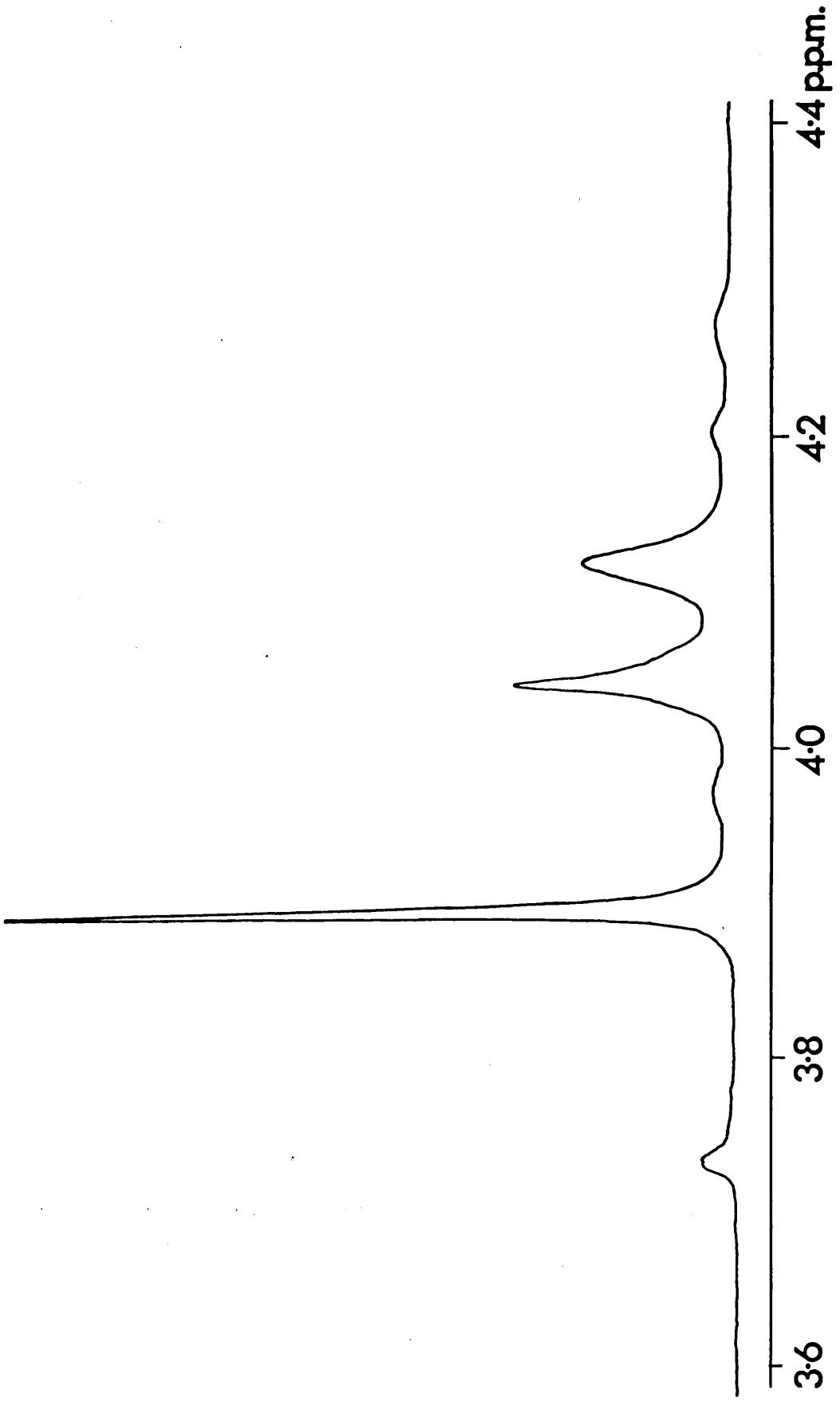

4·4 ppm.
4·2
4·0
3·8
3·6

Table XII: ^{1}H N.M.R. chemical shifts, $\delta\ ^{1}H$, and tin-proton coupling constants, $^{2}J(^{117,119}Sn - ^{1}H)$, and ^{119}Sn N.M.R. chemical shifts, $\delta\ ^{119}Sn$, of aqueous solutions of methyltin trichloride and its first hydrolysis product.

Compound	Concentration (M)	$\delta\ ^{1}H$[a] (p.p.m.)	$^{2}J(^{117,119}Sn-^{1}H)$ (Hz)	$\delta\ ^{119}Sn$[b] (p.p.m.)
$MeSnCl_3$	0.5	-3.98	127.9	-481
	0.25	-3.93	129.6	-486
	0.05	-3.89	130.2	-498
		-4.04	127.4	c
		-4.12	121.2	-515
	0.005	-3.93	~ 132	d
		-4.04	127.5	d
		-4.14	~ 119	d
$MeSnCl_2(OH).2H_2O$	0.1	-3.91	130.8	-487
		-4.04	126.4	c
		-4.11	120.9	c

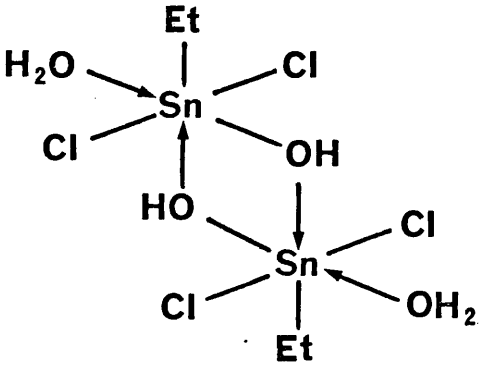
[a] Relative to the water resonance (- sign refers to upfield shift).

[b] Relative to Me_4Sn.

[c] Peak not detected.

d Not recorded.

has been shown[65] by X-ray crystallography to be



In order to establish that the general structure of the first hydrolysis products of the alkyltin trichlorides was the same as that of the ethyl derivative, a series of these compounds was prepared, by Luijten's method[50], and their melting points, analytical data and Mössbauer parameters are given in Table XIII. The close similarity of the Mössbauer parameters for the compounds prepared is indicative of the same 6 coordinate dimeric structure. The analytical results for the monomethyltin derivative (which has not been reported previously) suggest the presence of two water molecules. The second water molecule is, hence, most likely to be loosely bound, possibly by weak hydrogen bonds, e.g. $SnCl_4.5H_2O$[66].

A 400 MHz ^1H N.M.R. spectrum of a 0.1 M aqueous solution of $MeSnCl_2(OH).2H_2O$ very closely resembled that shown in Figure XXI, and a ^{119}Sn N.M.R. spectrum of the same solution

Table XIII: Melting points, analytical data and Mössbauer parameters of the first hydrolysis products of monoalkyltin trichlorides

Compound	M.P. (°C)	Analysis found (calcd.) % C	H	Cl	Mössbauer δ	ΔE_Q
$MeSnCl_2(OH).2H_2O$	69-77	3.96 (4.65)	3.10 (3.10)	27.60 (27.51)	0.84	2.13
$EtSnCl_2(OH).H_2O$	96-128 (94-6)[a]	9.37 (9.44)	3.05 (3.15)	27.60 (27.95)	0.96	2.23
$BuSnCl_2(OH).H_2O$	73-120 (80-7)[a]	16.57 (17.05)	3.69 (4.25)	25.57 (25.16)	0.89	2.38
$OctSnCl_2(OH).H_2O$	102-5 (45-56)[a]	28.33 (28.40)	5.66 (5.91)	21.60 (21.00)	0.89	2.23

[a] Ref. 50

revealed a peak at -487 p.p.m.. Again, other resonances may have been present, but were not detected above the noise level. The high field ^{119}Sn chemical shift is characteristic of a 6 - coordinate species and suggests that the dimeric structure does not break up in solution. From the N.M.R. observations it is therefore believed that the species formed upon dissolution of methyltin trichloride in water, at higher concentrations, is $MeSnCl_2(OH).2H_2O$.

Luijten[50] also prepared some second hydrolysis products of alkyltin trichlorides by reaction of 1 mole of the organotin trihalide with 2 moles of sodium hydroxide. The general formula of these compounds was found[50] to be $RSnCl(OH)_2.nH_2O$, where R = Et, Bu or Oct, and n = 0 or 1. Attempts to prepare and isolate in a pure state the second hydrolysis product of methyltin trichloride were unsuccessful. However, a 90 MHz ^1H N.M.R. spectrum of an aqueous mixture of 1 mole of methyltin trichloride and two moles of sodium hydroxide showed a broad peak centred at approximately 4 p.p.m. upfield from the water resonance, with broad $^{117,119}Sn$ satellites (presumably due to overlapping) of approximately 126 Hz coupling. This spectrum closely resembles the broad resonance seen in the ^1H spectrum of a 0.05 M aqueous solution of methyltin trichloride. It therefore appears that the second species formed upon dilution of an aqueous solution of methyltin trichloride is $MeSnCl(OH)_2.nH_2O$. The fact that the ^1H chemical shift of this species is upfield from that of $MeSnCl_2(OH).2H_2O$ indicates that the electronegativity of the OH groups is less than that of the Cl atoms. The magnitude of the coupling constant value, $^2J(^{117,119}Sn - {}^1H)$, is dependent[67] upon the % s character in the Sn-C orbital and,

since it is known[68] that electronegative groups repel s character, a less electronegative substituent will produce a decrease in $^{2}J(^{117,119}Sn - ^{1}H)$. Therefore, from the observed coupling constant values (Table XII), the peak at -4.12 p.p.m. may be assigned to $MeSnCl(OH)_2.nH_2O$. Consideration of the resonance intensities in Figures XX and XXI, also ascribes this peak to the second hydrolysis product.

The peak at -4.04 p.p.m. in Figure XXI must therefore be due to a third hydrolysis product. If it is assumed that, as before, this involves substitution of a Cl atom by an OH group, this would result in the formation of $MeSn(OH)_3$. Such a compound would presumably exist in aqueous solution, like the trimethyl- and dimethyl-tin species[46], in equilibrium with other hydroxy species.

i.e. $MeSn(OH)_3 \rightleftharpoons MeSn(OH)_2^{+} \rightleftharpoons MeSn(OH)^{2+} \rightleftharpoons MeSn^{3+}$.

A 0.05 M solution of methyltin trichloride has a pH of 1.4, and, therefore, $MeSn(OH)_3$ is unlikely to be present. Furthermore, the ^{1}H chemical shift argues against the aqueous species being $MeSn(OH)_3$, since this would have an even higher field chemical shift than $MeSnCl_2(OH).2H_2O$ or $MeSnCl(OH)_2.nH_2O$ on electronegativity grounds. It has been found[69] that the magnitude of the tin-proton coupling, $^{2}J(^{117,119}Sn - ^{1}H)$, in $\{Me_3Sn(H_2O)_2\}^{+}$ and $\{Me_2Sn(H_2O)_4\}^{2+}$ represents a % s character in each Sn-C orbital of 32% and 48% respectively. These values closely resemble those which would be expected for sp^2 (33% s) and sp (50% s) hybrid orbitals. In other words, the donation of electrons from the water molecules to tin does not

appear to affect the % s character in the Sn-C bonds. If the first and second hydrolysis products of methyltin trichloride are treated similarly, they can be assumed to be sp^3 hybridised, and would have a theoretical tin-proton coupling of approximately 52 Hz[68]. This is much less than the observed couplings of 130 Hz and 121 Hz (Table XII) and the difference must be due to an increase in % s character of the Sn-C orbital caused[67] by the electronegative Cl atoms or OH groups bonded to tin. From the observed couplings it may therefore be calculated that the increase due to a Cl atom is approximately 29 Hz, while that of an OH group is approximately 20 Hz.

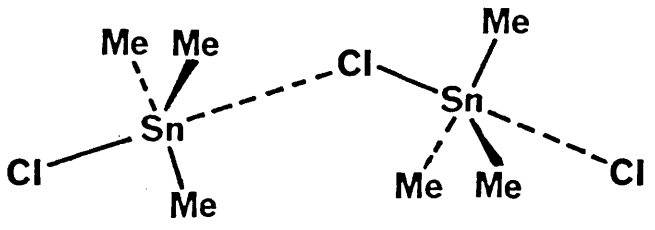
The coupling of 127 Hz recorded for the third hydrolysis product, indicates[67] a % s character in the Sn-C orbital of approximately 60%. Hence, if again the electron donating water molecules are ignored, the peak at -4.04 p.p.m., in Figure XXI, is clearly not due to the RSn^{3+} cation. In fact, it may be calculated that the 127 Hz coupling is similar to that which would be given by the $MeSn(OH)^{2+}$ ion (123 Hz). An ionic species, such as this, would undoubtedly be hydrated and it is therefore suggested that the peak at -4.04 p.p.m. in Figure XXI is predominantly due to $\{MeSn(OH)(H_2O)_4\}^{2+}$.

A 400 MHz ^1H N.M.R. spectrum of a 0.005 M aqueous solution of methyltin trichloride showed the same three peaks, as illustrated in Figure XXI, although that at approximately -3.9 p.p.m., i.e. $MeSnCl_2(OH).2H_2O$ was greatly reduced in intensity, and the major peak at this concentration, was at -4.04 p.p.m., i.e. $\{MeSn(OH)(H_2O)_4\}^{2+}$.

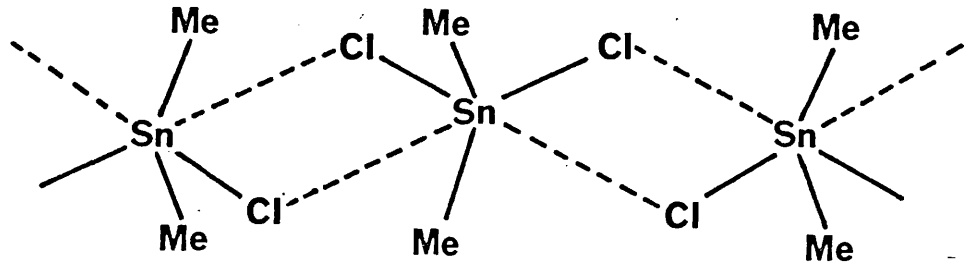
2.7. Summary

These studies have provided further evidence for the degradation of organotin compounds when exposed to U.V. light. However, it must be considered how the results obtained relate to the question of environmental degradation.

The studies of the breakdown of the methyltin chlorides in carbon tetrachloride (Section 2.4.1.) provided quantitative measurements of the relative rates of breakdown of the compounds, showing trimethyltin chloride to have the fastest breakdown rate and methyltin trichloride the slowest. The breakdown of tributyltin chloride in carbon tetrachloride (Section 2.4.2.) showed similar trends and so the results can probably be extended to other alkyltin compounds. However, the failing of these studies is that, firstly, carbon tetrachloride is a solvent that would not be encountered in the environment and, secondly, in such solutions, the organotin chlorides exist as discrete tetrahedral molecules, a geometric form that would not occur in a natural situation. For example, in water trimethyltin chloride and dimethyltin dichloride are known[46] to form ionic species, whilst, in the solid state, their coordination number is increased by bridging chlorine atoms. Trimethyltin chloride at 135 K has a coordination number of 5 and a chain structure[70] as shown below



whilst dimethyltin dichloride has a distorted trans-octahedral tin atom geometry[71].



These differences in structure and coordination number could very well affect the rates of breakdown. Furthermore, in carbon tetrachloride, the degradation products remained as chlorides, but, in the environment, this would not be the case. Nevertheless, the investigation of the degradation reactions in carbon tetrachloride provided valuable experience for studying a system that was more closely related to the environment, i.e. the U.V. degradation of methyltin compounds in water. (Section 2.4.3.).

This investigation demonstrated that tri-, di- and mono-methyltin compounds in aqueous solution break down, when irradiated with U.V. light, to produce the non-toxic species, stannic oxide. The formation of the dimethyltin cation from the trimethyltin cation is important, since this species will remain in solution and degradation will continue. If the insoluble dimethyltin oxide had been produced, precipitation would have

occurred and the rate of breakdown would have been greatly reduced. The pH values of the solutions irradiated were within the range 1.4 - 3.6. Obviously, from an environmental point of view, it would have been preferable to investigate the breakdown at neutral pH. Unfortunately, it was found that, at a concentration of 0.05 M, the dimethyltin species was only soluble at a pH value of less than 4, and so the studies were made under acidic conditions. However, it is not expected that pH will drastically affect the degradation process.

The trimethyltin cation, in water, when irradiated with U.V. light of wavelengths greater than 200 nm was seen to break down through cleavage of one and two Sn-C bonds. However, sunlight consists mostly of light above 300 nm.,[56] which is of lower energy. Thus, although it was demonstrated that breakdown would occur from irradiation with these higher wavelengths, it might be expected that the process would occur almost entirely by cleavage of just one bond at a time. It is difficult to evaluate the intensity of sunlight at the earth's surface, due to changing weather conditions and amounts of ozone, carbon dioxide and water vapour etc. But it has been estimated[73] that, when the sun is perpendicular to the earth's surface, the total irradiation intensity is approximately 92 mwatts cm^{-2}. Of this total light intensity, wavelengths between 300-400 nm. account for only 4-5% i.e. an intensity of approximately 4 mwatts cm^{-2}. This value is lower than that used for the degradation studies, and so the half-life for the breakdown would be correspondingly longer in the natural situation.

In the study of the aqueous breakdown of the trimethyltin cation, no monomethyltin species was detected in solution, although it was suggested that such a species was produced, but was breaking down with a rate comparable to its formation. From the investigation of the hydrolysis products of the monomethyltin trichlorides (Section 2.6.), it may now be suggested that this species was a monomethyltin ion, such as $\{MeSn(OH)(H_2O)_4\}^{2+}$.

Although the aqueous degradation study was only performed upon the methyltins, the breakdown procedure probably reflects that of the trialkyltins in general. The very low solubility of, for example, the tributyltins has prevented their precise structure in aqueous solution from being established. However, it is possible that hydrated ions are present, as with the methyltins, and the fact that tributyltin ethanesulphonate has been shown to form the hydrated tributyltin cation (Section 2.5.) provides some evidence for this. Therefore, just as the breakdown of tributyltin chloride, in carbon tetrachloride, paralleled that of trimethyltin chloride, so too might the breakdown of the tributyltin cation be similar to that of the trimethyltin cation.

The fact that the methyltin chlorides in aqueous solution have been shown to degrade to inorganic tin when irradiated with U.V. light is of obvious importance with regard to the possibility of the environmental methylation of inorganic tin, although the question of methylation must not be forgotten. Until it is known for certain whether methylation does or does not occur, and, if so, whether the rate of formation of methyltin compounds is fast or slow compared to their breakdown, much more work must be carried out in this field.

Finally, it must be remembered that U.V. degradation will only occur if light is absorbed by the organotin. The investigations discussed were all carried out in clear solvents, free from impurities. Natural water systems will almost certainly contain varying amounts of suspended particles of matter which will cut out irradiating light. Thus, below a certain depth, no U.V. degradation will occur, and, overall, the rate of breakdown could be drastically reduced. U.V. irradiation is, however, only one of the possible mechanisms that can induce degradation, and, in such circumstances, breakdown could still be occurring, due to, for example, microbial metabolism.

2.8. Experimental

The source of irradiation for the degradation studies was provided by a Hanovia U.V.S. 500 system. This utilises a medium pressure mercury arc tube, of 700 nm. internal pressure, with an arc output of 375-480 mwatts. The spectral range of such tubes extends upwards of 185 nm. However, wavelengths below 200 nm. were disregarded in this work, since such light is absorbed by air. In order that irradiations with wavelengths above 235 nm. could be performed, a so called "ozone-free" lamp was used. This is similar to the lamp described above, except that the quartz tube contains a filter which cuts out wavelengths below 235 nm. If the emission intensity at 254 nm. (the principle mercury line at low pressure is taken as unity, the approximate relative emission intensities of some different wavelengths

from a lamp of this type are given below[73]:

Wavelength (nm.)	Relative intensity
254	1.00
265	0.72
297	0.51
303	1.05
313	2.18
365	3.18
405	1.36
436	2.09
546	2.23

These wavelengths are only the major lines in the mercury spectrum at the given pressure. Emission also occurs at wavelengths between the above values, but at a much reduced intensity. For example the emission at 185 nm. is approximately 5% of that at 254 nm.[73].

Solutions to be irradiated were contained in silica cells (Spectrosil grade silica; U.V. cut-off = 170 nm.), arranged in an arc approximately 20 cm from the mercury tube, which was mounted vertically so as to give an even irradiation distribution in the horizontal plane. Condensers were attached to the sample cells, so as to prevent loss of solvent occurring during irradiation. It was possible to irradiate up to 6 samples simultaneously. However, small differences occurred in the light intensity received by each sample, due to varying amounts of reflected light and

the difficulty in positioning each cell exactly the same distance from the lamp. Although for short irradiation times these effects were negligible, they became apparent as the reaction proceeded. This could be seen in the increase in the standard deviation of the measured mean concentrations for longer irradiation times.

For the study of the breakdown of tributyltin chloride in carbon tetrachloride, the intensity of irradiation at the sample position was measured using a potassium ferrioxalate actinometer, which covers the range 200-400 nm. All other intensity readings were made with U.V. Products Ltd., 'Blak-ray', U.V. intensity meters, which cover the wavelength ranges 200-300 nm. and 300-400 nm..

The volume of solution irradiated was different for each of the three systems studied. For the methyltin chlorides in carbon tetrachloride, 3-4 cm^3 of solution were irradiated for each sample, whilst, for the butyltin chlorides in carbon tetrachloride, 6 cm^3 were irradiated. This was due to a greater volume of solution being required to obtain ^{119}Sn N.M.R. spectra than ^1H N.M.R. spectra. The study of the degradation of the methyltins in water (Section 2.4.3.) required a starting volume of 10 cm^3, since some solution was lost during each transfer for centrifuging.

^1H N.M.R. spectra for the degradation of the methyltins in carbon tetrachloride and water were recorded on a Perkin Elmer R 10 continuous wave N.M.R. spectrometer operating at a ^1H frequency of 60 MHz. Samples were contained in 5 mm. tubes and quantitative measurements of concentration were made by integration of the N.M.R. signal and also by comparison of

peak heights to those obtained from standard solutions.

^{119}Sn N.M.R. spectra obtained for the study of the butyltin chlorides in water were recorded on the Fourier transform N.M.R. spectrometer at Royal Holloway College. This spectrometer is based on a Varian HA60-IL magnet and has been converted to operation in the Fourier transform mode by Dr. D.G. Gillies. ^{119}Sn spectra were obtained at 22.37 MHz in 12 mm. tubes using a deuterium lock. Quantitative measurements were made by comparison of signal-to-noise ratios recorded for samples to those of standard solutions, obtained under identical conditions.

For the investigation of the monoalkyltin species in aqueous solution, 90 MHz ^{1}H and 33.34 MHz ^{119}Sn N.M.R. spectra were recorded on a JEOL FX90Q instrument using 10 mm. tubes and an internal deuterium lock on approximately 50% deuterium oxide. ^{119}Sn N.M.R. spectra were recorded using nuclear Overhauser suppressed conditions (Section 1.5.1.6.). 400 MHz ^{1}H N.M.R. spectra were recorded on a Bruker WH400 instrument in 5 mm. tubes with a similar deuterium lock.

^{119m}Sn Mössbauer spectra were recorded using a constant acceleration microprocessor spectrometer (Cryophysics Ltd., Oxford) with a 512-channel data store. The samples were placed in perspex disc holders, which were cooled to 80 K. The errors in δ and ΔE_Q are $\pm$ 0.05 mm. sec^{-1}.

U.V. absorbtion spectra were recorded on a Bausch and Lomb, Spectronic 505, double beam spectrophotometer.

2.9. References

1) R.S. Braman and M.A. Tompkins, Anal.Chem., 1979, 51, 12.

2) V.H. Hodge, S.L. Seidel and E.D. Goldberg, Anal. Chem., 1979, 51, 1256.

3) W.P. Ridley, L.J. Dizikes and J.M. Wood, Science, 1977, 197, 329.

4) L.J. Dizikes, W.P. Ridley and J.M. Wood, J. Amer. Chem. Soc., 1978, 100, 1010.

5) J.M. Wood, A. Cheh, L.J. Dizikes, S. Rakow and J.R. Lakowicz, Fed. Proc., 1978, 37, 16.

6) C. Huey, F.E. Brinckman, S. Grim and W.P. Iverson, Proc. Int. Conf. Transp. Persistant Chem. Aquat. Ecosyst., 1974, 73.

7) P.J. Craig, Environ. Technol. Lett., 1980, 1. 225.

8) R.C. Poller, 'The Chemistry of organotin Compounds', Academic Press, New York, 1970.

9) P. Cenci and B. Cremonini, Ind. Sacc. Ital., 1969, 62, 313.

10) M.E. Getzendaner and H.B. Corbin J. Agric. Food Chem., 1972, 20, 881.

11) H. Akagi and Y. Sakagami, Koshu Eiseiin Kenkyu Hokoku 1971, 20, No.1.

12) R.D. Barnes, A.T. Bull and R.C. Poller, Pestic Sci., 1973, 4, 305.

13) F. Massaux, Café Cacao Thé, 1971, 15, (3), 221.

14) A.H. Chapman and J.W. Price, Int. Pest Control, 1972, 14, 11.

15) D. Kloetzer and U. Thust, Chem. Tech., 1976, 28, (10), 614.

16) D. Kloetze, Zentra. Inst. Kernforsch. Rossendorf Dresden Zkf., 1977, (340), 84.

17) V.F. Komora and M. Popl, Holztechnol., 1978, 19, 3.

18) V.T. Mazaev, O.V. Golovanov, A.S. Igumnov and V.H. Tsay, Gig. Sanit., 1976, 17.

19) C.J. Soderquist and D.G. Crosby, J. Agric. Food Chem., 1980, 28, 111.

20) T. Man-Wing, Ph.D. Thesis, Univ. of London, 1978.

21) P. Dunn and D. Oldfield, Austral. Def. Sci. Ser., Technical Note 298.

22) W.P. Neumann, in 'The Organic Chemistry of Tin', Wiley, New York, 1970.

23) D. Barug and J.W. Vonk, Pestic. Sci., 1980, 11, 77.

24) E.H. Blair Environ. Qual. Saf. Suppl., 1975, 3 406.

25) B.G. Henshaw, R.A. Laidlaw, R.J. Orsler, J.K. Carey and E.G. Savory, Record of the 1978 Annual Convention of the B.W.P.A., 1978, 19.

26) L.E. Wise, in 'Wood chemistry', 1952, 1.

27) J.E. Cremer, Biochem. J., 1958, 68, 685.

28) J.E. Casida, E.C. Kimmel, B. Holm and G. Widmark, Acta. Chem. Scand., 1971, 25, 1497.

29) J.W. Bridges, D.S. Davies and R.T. Williams, Biochem. J., 1967, 105, 1261.

30) E.C. Kimmel, R.H. Fish and J.E. Casida, J. Agric. Food Chem., 1977, 25, 1.

31) E.H. Blair, Environ. Qual. Saf. Suppl., 1975, 3, 406.

32) K.D. Freitag and R. Bock, Pestic. Sci., 1974, 5, 731.

33) J.J. Zuckerman, in 'Organometals and Organometalloids : Occurrence and Fate in the Environment', A.C.S. Symp. Ser., 1978, 82, 388.

34) A.W. Sheldon, J. Paint Technol., 1975, 47, 54.

35) P.J. Smith, A.J. Crowe, D.W. Allen, J. Brooks and R. Formstone, Chem. Ind. (London), 1977, 874.

36) V.S. Petrosyan, Prog. in N.M.R. Spectrosc., 1977, 11, 115.

37) E.V. Van den Berghe and G.P. Van der Kelen, J. Organomet. Chem., 1966, 6, 522.

38) G.A. Razuvaev, N.S. Vyazankin, E.N. Gladyshev and I.A. Borodavko, Zh. Obshch. Khim., 1962, 32, (7), 2154.

39) D.J. Williams and J.W. Price, Analyst, 1964, 89, 220.

40) J.D. Roberts and M.C. Ceserio, in 'Basic Principals of Organic Chemistry', W.A. Benjamin, Inc., New York, 1965.

41) G. Stephenson, in 'Mathematical Methods for Science Students', Longman Groups Ltd., London, 1961.

42) J.R. Cavanaugh and B.P. Dailey, J. Chem. Phys., 1961, 34, 1099.

43) A.G. Davies, Personal communication.

44) P.J. Smith and A.P. Tupciauskas, Ann. Reps. of N.M.R. Spectrosc., 1978, 8, 291.

45) R.H. Fish, E.C. Kimmel and J.E. Casida, J. Organomet. Chem., 1976, 118, 41.

46) R.S. Tobias, in 'Organometals and Organometalloids : Occurrence and Fate in the Environment', A.C.S. Symp. Ser., 1978. 82, 130.

47) F.E. Brinckman, G.E. Parris, W.R. Blair, K.L. Jewett, W.P. Iverson and J.M. Bellama, Environ. Health Perspect., 1977, 19, 11.

48) T.L. Sayer, S. Backs, C.A. Evans, E.K. Millar and D.L. Rabenstein, Can. J. Chem., 1977, 55, 3255.

49) M.M. McGrady and R.S. Tobias, Inorg. Chem., 1964, 3, (8), 1157.

50) J.G.A. Luijten, Rech. Trav. Chim. Pays-Bas, 1966, 85, 873.

51) C.J. Soderquist and D.G. Crosby, Anal. Chem., 1978, 50, 1435.

52) T.S.V. Bonehev, D. Khristov and B. Manushev, Z. Anorg. Allg. Chem., 1970, 379, 95.

53) M. Christianson, D. Price and R. Whitehead, J. Organomet. Chem., 1975, 102, 273.

54) V.A. Nazarenko, V.P. Antonovich and E.M. Nevskaya, Russ. J. Inorg. Chem., 1971, 16, 980.

55) F.A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry", 3rd edition, p.326. Interscience Publishers, London, 1972.

56) D.A.M. Watkins, Chem. and Ind., 2 March, 1974.

57) Anon., Albright and Wilson, Technical Note.

58) A.H. Meyling and R.J. Pitchford, Bull. Wld. Health, 1966, 34, 141.

59) S.J. Blunden, A.H. Chapman, A.J. Crowe and P.J. Smith, Int. Pest. Control, July/Aug. 1978, 20, 5.

60) R. Suzuki, Y. Kuriyama and H. Shioyama, Jap. Pat., 18489, 1976.

61) M. Nakanishi and A. Tsuda, Brit. Pat., 1,099, 704, 1968.

62) R. Hill, Unpublished result.

63) P.G. Harrison, R.C. Phillips, and J.A. Richards, J. Organomet. Chem., 1976, 114, 47,

64) E.V. Van den Berghe and G.P. Van der Kelen, Bull. Soc. Chim. Belg., 1965, 74, 479.

65) C. LeCompte, J. Protas and M. Devaud, Acta. Cryst., 1976, B32, 923.

66) J.C. Barnes, H.A. Simpson and T.J.R. Weakley, J. Chem. Soc. Dalton Trans., 1980, 949.

67) C.S. Hoad, R.W. Matthews, M.M. Thakur and D.G. Gillies, J. Organomet. Chem., 1977, 124, C31.

68) H.A. Bent, J. Inorg. Nucl. Chem., 1961, 19, 32.

69) J.R. Holmes and H.D. Kaesz., J. Amer. Chem. Soc., 1961, 83, (18), 3903.

70) M.B. Hossain, J.L. Lefferts, K.C. Molloy, D. Van der Helm and J.J. Zuckerman, Inorg. Chim. Acta., 1979, 36, L409.

71) A.G. Davies, H.J. Milledge, D.C. Puxley and P.J. Smith, J. Chem. Soc., 1970, A, 2862.

72) Anon., Oriel Solar Simulators, Technical note.

73) Anon., Hanovia Lamps Ltd., Technical note.

CHAPTER 3

THE DETERMINATION OF ORGANOTIN COMPOUNDS BY SPECTROFLUORESCENCE

3.1. Introduction

The U.V. degradation studies described in Chapter 2 were carried out upon solutions of relatively high concentration due to the difficulties involved in the analysis of compounds at the sub-p.p.m. level. A selection of the analytical techniques employed for the determination of organotin compounds at sub-p.p.m. levels were discussed in Section 1.6. Of these methods, however, some, e.g. anodic stripping voltammetry[1], require rather elaborate instrumentation, while other methods, such as chromatographic separation[2] and photometric analysis[3], are long and time-consuming. By comparison, spectrofluorescence is a relatively simple and rapid technique, yet, nevertheless, possesses the qualities of extreme sensitivity and good specificity. The sensitivity of spectrofluorescence is often observed to be 100 times greater than corresponding absorption photometric methods[4]. The reason for this increased sensitivity is that, in fluorescence, the emitted radiation is measured directly, whereas, in photometric techniques, the absorbed radiation is measured indirectly as the difference between the incident and transmitted beams. Thus, in absorption photometry,

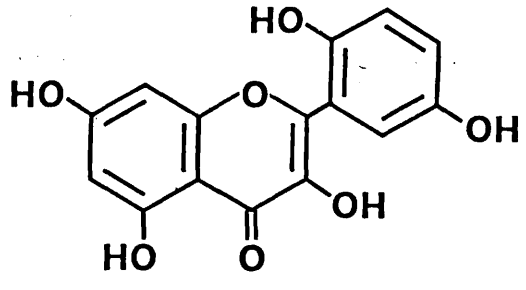
a very small change in a large signal is measured and so a loss in sensitivity is consequently experienced.

The high specificity of spectrofluorescence arises from two factors; a) fewer compounds fluoresce than absorb, because all fluorescent compounds absorb radiation, but not all absorbing compounds emit radiation, and b) two wavelengths are used in fluorescence but only one in absorption.

Spectrofluorescence has found wide application as an analytical technique in the medical and biochemical fields, where many naturally occurring molecules exhibit fluorescent properties, but, as yet, the technique is not used to the same extent in the chemical laboratory. The potential of spectrofluorescence, however, as a very sensitive, yet relatively inexpensive means of analysis, warrants further investigation into the use of the method for the determination of tin and organotin compounds at sub-p.p.m. levels.

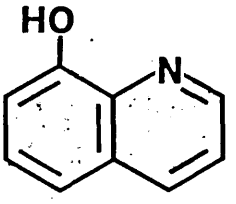
3.2. Review of fluorescent methods for the determination of inorganic tin and organotins.

The recent developments in the spectrofluorimetric analysis of organotins have arisen from previous work on the determination of inorganic tin using fluorescent reagents. In 1953, Patrovsky[5] reported a method for detecting tin by observation of the green fluorescence produced with morin,



(Morin)

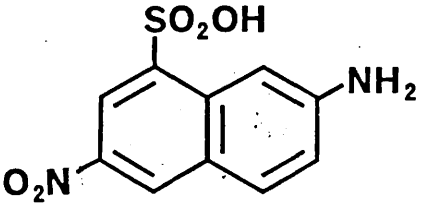
and this method was later adapted by Ginzberg[6] for the determination of tin in ores at levels as low as 10 p.p.m.. In the same work, Ginzberg[6] also reported a fluorescent complex formed from tin and 8-hydroxyquinoline.



(8-hydroxyquinoline)

The intensity of fluorescence from this complex was, however, less than that produced with morin and the method was therefore not as sensitive.

Anderson and Garnett[7] noted that stannous tin, when reacted with the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid, produced a blue fluorescence when irradiated with U.V. light.

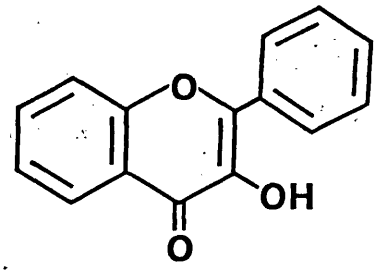


(6-nitro-2-naphthylamine-8-sulphonic acid)

This reaction was applied[8] to the determination of tin in copper base alloys, the tin being determined within the range 0.2 - 2.0 p.p.m.. It was found that, of 47 ions investigated, the reagent was specific for stannous tin. However,

many ions interfere with the determination and so the stannous tin had first to be separated from other cations present. The method was also difficult to apply, since the total tin had first to be reduced to stannous ions and fluorescent measurements made under an atmosphere of CO_2, to prevent oxidation to stannic tin.

Coyle and White[9] developed a method for the analysis of tin at concentrations as low as 0.1 p.p.m. using 3-hydroxyflavone.



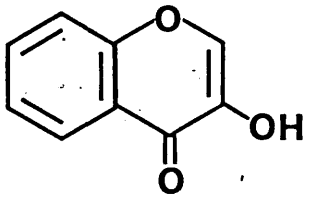
(3-hydroxyflavone)

The effect of pH was investigated[9] and was found not to drastically affect the fluorescence intensity. In addition, very few ions were found to interfere with the determination only zirconium, molybdenum, hafnium, phosphate, fluoride and chloride having a serious effect.

Pal and Ryan[10] reported a more sensitive method for the determination of tin (0.005 - 0.25 p.p.m.) using 8-hydroxyquinoline-5-sulphonic acid as the fluorescent reagent.

and is claimed to have a detection limit of approximately 0.0003 p.p.m. of tin, although the minimum quantity of tin that can be determined with a precision of about 10% is 0.0008 p.p.m.. Antimony, zirconium, hafnium, aluminium, gallium, tungsten, molybdenum, niobium and tantalum interfere in the direct determination. A slight disadvantage of this method is that the reagent, 3,4',7-trihydroxyflavone, is not at present commercially available and must be prepared according to published procedures[12].

Nakamura and Murata[13] reported a fluorescent determination for tin using 3-hydroxychromone.



(3-hydroxychromone)

Tin could be determined at concentrations as low as 0.015 p.p.m., and, although this sensitivity is not as high as that given by other methods[9-11], chloride ions at concentrations of up to 12 mg cm^{-3} did not affect the analysis.

The first report of a fluorimetric determination of an organotin compound was by Vernon[14], who used 3-hydroxyflavone for the determination of triphenyltin residues in potatoes in the range 0.001 - 0.003 p.p.m.. The method[14] was specific for

triphenyltin compounds and it was found that mono- and diphenyltin compounds and inorganic tin did not interfere with the procedure. Vernon's method[14] has since been applied to the determination of triphenyltin compounds in water[15] (Section 3.3) and on a wider range of substrates[16]. 3-hydroxyflavone has also been reported as being a suitable reagent for the determination of trimethyltin compounds[17], the minimum concentration of trimethyltin that could be determined being 0.015 p.p.m. and Huey[18] used the same reagent for the qualitative detection of di- and mono-methyltin species.

3.3. Spectrofluorescent determination of triphenyltin compounds in water.

Triphenyltin acetate and hydroxide are used as fungicides for the control of the potato blight fungus, Phytophthora infestans, and as biocides in some marine antifouling paints (Section 1.4.). Owing to the manner in which the compounds are applied as fungicides, by aerial spraying, there is the possibility that ponds, streams and rivers could be contaminated, either by an air-borne spray or by run-off water from fields adjacent to waterways. For marine antifouling systems, where leaching of trace amounts of the compound into sea-water is inevitable, contamination could again occur. Unfortunately, triphenyltin compounds are relatively toxic to aquatic life[19] {96 hr LC_{50} = 0.015 p.p.m. (rainbow trout fry)} and, thus, the determination of these compounds at sub-p.p.m. levels is obviously important.

Vernon[14] had developed a method for the determination of triphenyltin compounds in potatoes using 3-hydroxyflavone (Hof), and it was

therefore decided to use this fluorescent reagent for determining triphenyltin compounds in water.

Initially, the excitation and emission wavelengths of a number of methyl-, butyl-, and phenyl-tin/3-hydroxyflavone complexes, and of the reagent itself, were established by adding 1 cm^3 of a 5 x 10^{-6} M solution of the organotin to 5 cm^3 of a 0.01% 3-hydroxyflavone solution in toluene, and measuring the excitation and emission wavelengths on the spectrofluorimeter (see Table I).

Table I: Maximum excitation and emission wavelengths of 3-hydroxyflavone (Hof), some organotin/Hof complexes and the $SnCl_4$/Hof complex.

Compound	Excitation wavelength (nm.)	Emission wavelength (nm.)
Hof	360	525
Ph_3SnOAc/Hof	395	495
Ph_3SnCl/Hof	395	495
Ph_2SnCl_2/Hof	395	450
$PhSnCl_3$/Hof	395	450
Me_3SnCl/Hof	395	510
Me_2SnCl_2/Hof	395	450
n-Bu_2SnCl_2/Hof	395	450
$SnCl_4$/Hof	395	450

Triphenyl- and trimethyl-tin compounds were found to have specific emission wavelengths. However, tri-n-butyltin

compounds did not form a fluorescent complex with 3-hydroxyflavone under given conditions. This observation has since been confirmed by Aldridge[17], who extended the range of organotin/3-hydroxyflavone complexes and also investigated the triethyl-, tri-n-propyl-, n-octyldimethyl-, phenyldiethyl-, and ethyldiphenyl-tin compounds, but still the only R_3SnX compounds known to form fluorescent complexes with 3-hydroxyflavone are those in which R = Ph or Me. The R_2SnX_2, $RSnX_3$ and inorganic tin complexes were all found to emit at 450 nm. The emission from the R_2SnX_2 and $RSnX_3$ compounds, however, was unstable and calibration curves could not be drawn.

Vernon[14] reported that the fluorescent complexes formed from triphenyltin acetate or triphenyltin chloride and 3-hydroxyflavone had maximum emission wavelengths at 497 nm. and 450 nm. respectively, a fact which could not be understood, in view of both organotins forming a 1:1 complex with the reagent. In the present work, the emission at 450 nm., claimed[14] to be due to the triphenyltin chloride/3-hydroxyflavone complex, was not observed, and, in fact, both triphenyltin chloride and acetate produced complexes with a maximum emission at approximately 495 nm. The intensity of emission from the triphenyltin/3-hydroxyflavone complexes was, however, found to be unstable, and a solution which had been left standing, even in the subdued light of the laboratory for approximately 1 hour, was found to have an emission which had changed from 495 nm. to an emission of much weaker intensity at approximately 465 nm. The instability to light of organotin complexes was first documented by Aldridge and Cremer[20], and, although not mentioned by Vernon[14], it was found to be essential to keep the solutions in flasks that were covered with black

paper, both before and after addition of the reagent to the triphenyltin solution. It was observed, however, that, even when kept in the dark, the emission from the complex formed from triphenyltin chloride was unstable, whereas the emission of the complex from triphenyltin acetate was stable over a number of hours. This effect was found to be due to the presence of chloride ions, which quenched the fluorescence emission, but the problem was easily overcome by shaking the solution with 1 cm^3 of saturated aqueous sodium acetate. Care had to be taken to ensure that contamination of the solution by chloride ions did not occur after separation from the aqueous sodium acetate layer. It was found, for example, that contamination could very easily arise by cleaning the sample cuvettes with hydrochloric acid. Thus, it was important to ensure a thorough rinsing of the cuvettes before fluorescence measurements were made. Shaking the solution with saturated aqueous sodium acetate had one other very important effect, since acetate was found to quench the fluorescence of R_2SnX_2, $RSnX_3$ and inorganic Sn/3-hydroxyflavone complexes. In fact no fluorescent species was produced if, for example, diphenyltin diacetate was mixed with 3-hydroxyflavone in toluene, whereas a fluorescent complex was formed if diphenyltin dichloride was used instead. The emission intensity produced from the latter compound was, however, unstable and this may again have been due to the presence of chloride ions in solution. Consequently, it is because of the quenching effect of acetate that triphenyltin compounds may be determined in the presence of an excess of diphenyltin, monophenyltin or inorganic tin species. It was found that at least a 10 molar excess of these compounds had no effect on the determination of triphenyltin. Perhaps the only organotin compounds which

would interfere with the determination are the trimethyltins. Although the emission maximum of the trimethyltin/3-hydroxyflavone complex is at approximately 510 nm., this is not sufficiently different from the triphenyltin emission at approximately 495 nm. for these compounds to be determined in the presence of each other.

The excitation wavelength producing a maximum emission for the triphenyltin complexes was found to be approximately 395 nm. However, this wavelength still produces some emission from 3-hydroxyflavone at 525 nm., and, at low organotin concentrations, this could interfere with the determination. Therefore, the excitation wavelength chosen for the quantitative determination of triphenyltin was 415 nm., since, although this resulted in a slightly reduced emission intensity at 495 nm., the interference from the 3-hydroxyflavone emission was vastly reduced. An excitation wavelength of 415 nm. was also found to be suitable for trimethyltin determinations.

Barnes et al.[21] showed that triphenyltin acetate hydrolyses rapidly to the hydroxide in the presence of a large amount of water and, thus, any solubility figures for triphenyltin acetate in water are likely to correspond to the hydrolysed product. This figure was found[21] to be approximately 3 p.p.m. in distilled water. At this level, triphenyltin may be readily extracted from water by shaking with toluene[22]. Therefore, the analytical procedure developed for the determination of triphenyltin compounds in water was as follows:-

50 cm^3 of the water sample were shaken with 10 cm^3 of toluene in a separating funnel for approximately 30 minutes and the two layers then allowed to separate.

For the determination of triphenyltin compounds in the range 0.2 - 2.0 p.p.m., 1.0 cm^3 of the toluene layer was added to 5.0 cm^3 of a 0.01% solution of 3-hydroxyflavone in toluene and 1 cm^3 of a saturated aqueous solution of sodium acetate in a stoppered container (e.g. a 10 cm^3 calibrated flask) covered with black paper and shaken for approximately 10 minutes. The fluorescence emission at approximately 495 nm., of the organic layer was measured using an excitation wavelength of approximately 415 nm. For the 0.004 - 0.2 p.p.m. range of triphenyltin compounds, 5.0 cm^3 of the toluene layer were added to 1.0 cm^3 of the 3-hydroxyflavone solution and 1 cm^3 of saturated aqueous sodium acetate solution and the method continued as above. A reagent blank was prepared by shaking 50 cm^3 of water free from triphenyltin with 10 cm^3 of toluene and the method again continued as before.

Calibration graphs were prepared by mixing known volumes of triphenyltin chloride solutions (5×10^{-7} - 5×10^{-5} M) in toluene with either 1.0 or 5.0 cm^3 (as appropriate) of a 0.01% solution of 3-hydroxyflavone in toluene and the volume made up to 6.0 cm^3. This solution was shaken with 1 cm^3 of saturated aqueous sodium acetate solution in a darkened container for approximately 10 minutes and the fluorescence emission measured as before.

— — — — — — — —

An analytical procedure cannot be considered useful if the technique is only successful when determining a species from 'clean' laboratory solutions. It must be possible to apply

the technique to the determination of the species in 'real' samples, in which there may often be many impurities present. Therefore, samples of distilled water, tap water, canal water and synthetic sea water (prepared according to BS 3900 : Part F4)[23] were spiked with standard solutions of triphenyltin chloride in ethanol. The organotin was then extracted and determined using the above procedure. It was found that the method is equally applicable to the determination of triphenyltin compounds in all types of water, and that reagent blank values were not significantly higher than for distilled water. Results of the extraction and determination procedure from all types of water at different concentrations are given in Table II and show that the average percent recovery of triphenyltin over the range 2.0 - 0.004 p.p.m., fell from 93.6% to 78.6%. However, at such a low concentration as 0.004 p.p.m., a recovery of almost 80% is considered to be adequate.

Large reagent blank values were sometimes obtained from some samples of toluene. This effect was attributed to light scatter from immiscible impurities in the solvent, although these were not water droplets and did not arise from impurities in the water. The effect of the solvent grade upon the reagent blank was therefore investigated and Table III shows average blank readings which were obtained with the spectrofluorimeter set to read 0 and 300 on the emission scale for calibration 0 - 0.1 μg of triphenyltin per 6 cm^3.

It can be seen that significantly lower blank readings were obtained from Aristar grade toluene compared to AnalaR grade. The standard deviation of the blank value is also reduced. The effect of improving the blank readings by using Aristar grade

Table II: Recoveries of triphenyltin chloride from water.

Concentration of triphenyltin, p.p.m.	Solvent grade	No. of extractions (all types of water)	Average recovery %	Standard deviation σ_{N-1}, %
2.0	AnalaR	7	93.6	3.2
0.2	AnalaR	18	89.4	4.9
0.02	AnalaR	4	88	10.0
0.008	AnalaR	10	82.9	11.9
0.004	AnalaR	17	74.0	11.3
0.004	Aristar	16	78.6	8.9

Table III: Effect of the solvent grade on the reagent blank.

Solvent grade	No. of readings (all types of water)	Average blank	Standard deviation σ_{N-1}, %
AnalaR	11	13.8	17.8
Aristar	20	4.4	7.7

toluene is illustrated in Table II, where determinations were made at the 0.004 p.p.m. level using both grades of toluene, and it is noted that the determinations made in the purer solvent showed an increase in the average percent recovery recorded and a corresponding decrease in standard deviation.

This work has therefore shown that triphenyltin compounds in water at concentrations of 0.004 - 2 p.p.m. are readily extracted into toluene and can be determined by spectrofluorimetric measurement of the triphenyltin/3-hydroxyflavone complex. Although it appears that a similar method might be developed for trimethyltin compounds, the reagent does not seem to be suitable for the specific determination of R_2SnX_2 or $RSnX_3$ compounds.

3.4. Spectrofluorescent determination of the total organotin concentration in water.

The previous section discussed the development of a method for the determination of triphenyltin compounds in water. However, another analytical procedure which would be of use, is one in which the total organotin concentration in aqueous solution may be determined relatively simply by spectrofluorescence. Since a reagent possessing similar fluorescence properties for all organotins is not known, the method would have to incorporate the following stages:

a) extraction of the organotin compounds from the water sample.

b) wet-ashing with sulphuric/nitric acids, to convert the organotins to inorganic tin.

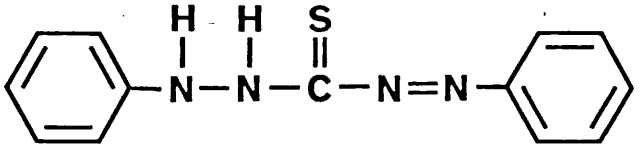
c) complexing the inorganic tin with a fluorescent reagent and quantitative measurement of the tin present.

The fluorescent method which was chosen for the final determination of inorganic tin was that of Coyle and White[9], which again uses 3-hydroxyflavone as the fluorescent reagent.

Initial work was carried out to ensure that very small amounts of tin (~ 1 µg) could be recovered from beakers, as if a sample had been wet-ashed. Thus, 1 µg of tin in solution in 1.5 M H_2SO_4 was added to 150 cm^3 beakers with 0.5 cm^3 Aristar H_2SO_4. The sulphuric acid was then evaporated off and the 1 µg of tin redissolved in 7.5 cm^3 dimethylformamide (DMF) and 1 cm^3 1.5 M H_2SO_4, these being the solvent solutions used in the method of Coyle and White[9]. The solution was then transferred to a 25 cm^3 graduated flask, 2 cm^3 of 0.05% 3-hydroxyflavone in ethanol were added and the solution made up to the mark with water. The fluorescence emission, at 450 nm, of the solution was then measured, using a 395 nm excitation wavelength, and compared to standard solutions. This revealed that, on average, approximately 80% of the tin was recovered.

It was during this preliminary work that the problem of contamination was encountered. Samples which had been evaporating on a hot-plate were often found, by fluorescence, to contain far more than the 1 µg of tin which had been added. Thus, great care had to be taken to avoid contamination, and samples were evaporated under cover to prevent dust falling into the beakers.

Triphenyltin compounds readily extract from water into toluene. However, not all organotins extract from water so easily and a better technique for general use with organotins is to extract the compound as the organotin/dithizone complex[20], by shaking the water sample with a 0.005% solution of dithizone in chloroform in the presence of a borate buffer.



(dithizone)

Thus, after establishing that 1 µg of tin could be retrieved with about 80% recovery, a few cm^3 of chloroform were added to the beakers, along with 1 µg of tin and 0.5 cm^3 of sulphuric acid, and the chloroform wet-ashed with nitric acid before determining the tin present as before. This process was also repeated with 2.5 µg of bis(tri-n-butyltin) oxide, TBTO, (contains ~ 1 µg tin) and again, in both cases, generally good recoveries were achieved.

For the extraction of the organotins from water, 20 cm^3 of dithizone/chloroform solution were to be shaken with 100 cm^3 of water. Therefore, in order to check that the dithizone did not interfere with the analytical determination, 2.5 µg of TBTO were added to 20 cm^3 of 0.005% dithizone in choroform, in 150 cm^3 beakers. 0.5 cm^3 Aristar sulphuric acid was then added and the majority of the solvent evaporated off before

nitric acid was added to wet-ash the sample. Once again, fluorescence revealed that generally good recoveries were achieved, but occasionally very low results were obtained.

Finally, the complete method was tested by taking 100 cm^3 of distilled water containing 1.5 µg TBTO, adding 20 cm^3 of buffer solution and shaking twice with 10 cm^3 of 0.005% dithizone in chloroform for 2 minutes. The chloroform layers were combined in a 150 cm^3 beaker and 0.5 cm^3 Aristar sulphuric acid added. Procedures for the wet-ashing and determination of tin were then continued as above. As before, although good percent recoveries were obtained, they were not always consistent.

Throughout all of this work, blank samples, free from tin, were analysed simultaneously with those containing tin, and a problem which arose was in obtaining consistent blank emission readings. This may still be due to contamination from air-borne particles during the wet-ashing procedure but, on occasions, blank samples which had undergone the complete determination procedure gave emission readings lower than those of a normal reagent blank. The reason for this is not understood, but the same cause may be responsible for the inconsistency in the percent recoveries obtained for the tin samples. However, a further investigation of this effect would need to be carried out before the method could be applied to the determination of organotins in 'real' samples.

3.5. Investigation of fluorescent reagents for phenyltin compounds, Ph_nSnX_{4-n}.

3-hydroxyflavone has been shown to be a suitable reagent for the fluorescent determination of inorganic tin[9], triphenyltin

compounds[14-16] and, trimethyltin compounds[15,17,18]. However, as yet, reagents are not known enabling the specific determination of any other organotin species.

The determination of diphenyl- and monophenyl-tin compounds would complement the analysis of triphenyltin species, described in Section 3.3, and would, for instance, permit the degradation of triphenyltin compounds at sub-p.p.m. levels to be studied. Consequently, a few compounds were briefly investigated to see whether they might act as suitable fluorescent reagents for the determination of phenyltin compounds, Ph_nSnX_{4-n}. Solutions of the reagent and the organotin were mixed and where fluorescence occurred the excitation and emission wavelengths were established and are given in Table IV.

8-hydroxyquinoline-5-sulphonic acid has been used as a fluorescent reagent for inorganic tin by Pal and Ryan[10]. However, no fluorescence was observed when organotins were substituted for inorganic tin and the procedure repeated.

Phenylfluorone, 0.001% in ethanol, did not form a fluorescent complex with triphenyltins, but did fluoresce with di- and monophenyltins. Therefore, it is possible that the reagent might be used along with 3-hydroxyflavone to determine a total concentration of phenyltin species. A lot more work needs to be carried out, however, to investigate this possibility.

Quercetin, 0.01% in toluene, was found to form a strongly fluorescent species with diphenyltin compounds. The intensity of fluorescence, however, was unstable and calibration graphs were not achieved. Acetate was found to quench the fluorescence and, if the solutions were prepared in ethanol, the fluorescence

Table IV: Excitation and emission wavelengths of some organotin / fluorescent reagent complexes.

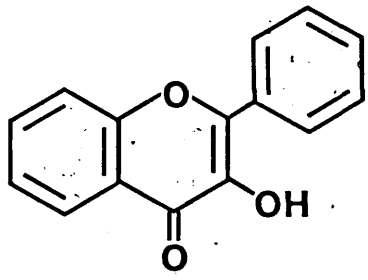
Reagent	Organotin	Excitation wavelength (nm)	Emission wavelength (nm)
Phenylfluorone	Ph_2SnCl_2	465	560
	$PhSnCl_3$	465	560
Quercetin	Ph_2SnCl_2	397	460
Morin	Ph_3SnCl	440	528
	Ph_2SnCl_2	440	507
	$PhSnCl_3$	440	503

intensity was vastly reduced. Once again, more work needs to be carried out to see if the emission can be stabilised, permitting the reagent to be used for diphenyltin determinations.

Morin was found to fluoresce with mono-, di- and tri-phenyltin compounds. However, the emission wavelengths are probably too close together for the compounds to be determined in the presence of each other.

3.6. Spectroscopic investigation of organotin/3-hydroxyflavone complexes.

3-hydroxyflavone (Hof; I) has been shown to form fluorescent complexes with both inorganic and organic tin compounds.



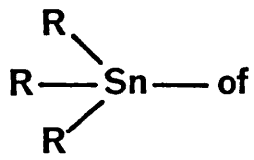
(I)

Although most organotins appear to form complexes with 3-hydroxyflavone in solution[17], not all are fluorescent and none have been isolated in the solid state. Consequently, a series of air stable organotin/3-hydroxyflavone complexes was prepared and their structures studied by ^{119m} Mössbauer,

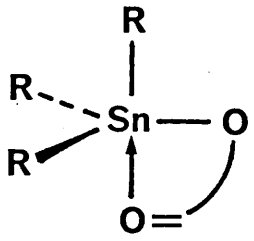
^{119}Sn N.M.R. and I.R. spectroscopy, in order to determine whether any relationships between structure and fluorescent properties could be established.

The ^{119m}Sn Mössbauer isomer shift, δ, and quadrupole splitting, ΔE_Q, parameters and the solid state antisymmetric carbonyl stretching frequencies, ν_{as} (CO), for the complexes are shown in Table V, and the ^{119}Sn N.M.R. chemical shifts, $\delta(^{119}Sn)$, and solution ν_{as} (CO) I.R. bands are given in Table VI.

The ΔE_Q values for the tributyl- and triphenyl-tin derivatives are consistent[24] with a tetrahedral tin atom geometry (IIa) or a pentacoordinate trigonal bipyramidal structure (IIb) with an intramolecularly coordinated carbonyl group.



(IIa)



(IIb)

However, the reduced ν_{as} (CO) frequencies observed for the complexes (Table V) are indicative of coordination to tin by the carbonyl group and so structure (IIb) is favoured. $Ph_3SnONPh.CO.Ph$ has been shown[25] by X-ray crystallography to adopt structure (IIb) and shows a ΔE_Q value of 1.94 mm sec^{-1},[26] which is similar to that of $Ph_3Sn(of)$ (see Table V). The ΔE_Q values of the tricyclohexyltin, Cy_3Sn, and trineophyltin, Np_3Sn, derivatives of 3-hydroxyflavone (Table V) are larger than are

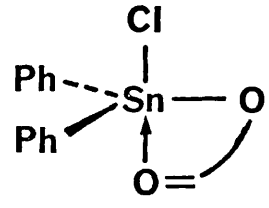
Table V: ^{119}Sn Mössbauer parameters and antisymmetric carbonyl stretching frequencies of the organotin/ 3-hydroxyflavone complexes

Complex	δ (mm sec^{-1})	ΔE_Q (mm sec^{-1})	ν_{as} (CO) (cm^{-1})
$Bu_3Sn(of)$	1.30	2.46	1574
$Ph_3Sn(of)$	1.08	1.90	1550
$Np_3Sn(of)$	1.34	2.59	1587
$Cy_3Sn(of)$	1.36	2.81	1574
$Ph_2SnCl(of)$	1.10	2.61	1530
$Ph_2Sn(of)_2$	0.77	1.75	1548
$Me_2Sn(of)_2$	1.09	3.09	1548
$Bu_2Sn(of)_2$	1.25	3.27	1550
$MeSnCl(of)_2$	0.71	1.77	1550

usually associated with structure (IIb),[24] but their reduced ν_{as} (CO) values are seen to be similar, both in the solid state and in solution (Tables V and VI) and, therefore, structure (IIb) is again favoured.

^{119}Sn N.M.R. chemical shifts are also indicative of coordination number, 5 coordinate compounds generally having a $\delta(^{119}Sn)$ value upfield of 4 coordinate species[27]. The triphenyltin derivative of dibenzoylmethane, $Ph_3Sn(bzbz)$, is known[28] to have the 5 coordinate trigonal bipyramidal structure (IIb) and has a $\delta(^{119}Sn)$ value of -82 p.p.m., and so the value of -149.8 p.p.m. recorded for $Ph_3Sn(of)$ is indicative of a similar geometry. The upfield shift of approximately 110 p.p.m. of $Np_3Sn(of)$ (51.4 p.p.m.) compared to the 4 coordinate Np_3SnOH (161 p.p.m.) also implies a coordination number of 5. Unfortunately, data is not at present available for similar comparison for $Cy_3Sn(of)$. The value of 70.5 p.p.m. for $Bu_3Sn(of)$ is at an unusually low field for 5 coordinate species, <u>c.f.</u> $Bu_3Sn(ox)$; $\delta(^{119}Sn)$ = 29 p.p.m.,[27] but other examples of low field ^{119}Sn chemical shifts for 5 coordinate species are known, <u>e.g.</u> $Me_3SnOCH_2CH_2NMe_2$; $\delta(^{119}Sn)$ = 92.1 p.p.m.[29]

The ΔE_Q value observed for $Ph_2SnCl(of)$ is indicative[24] of a trigonal bipyramidal <u>cis-</u> R_2SnX_3 tin atom geometry (III) with a chelating 3-hydroxyflavone ligand,



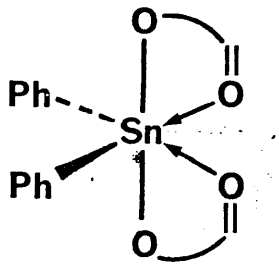
(III)

Table VI: ^{119}Sn chemical shifts and solution antisymmetric carbonyl stretching frequencies of the organotin/3-hydroxyflavone complexes.

Complex	Solvent	Concentration (M)	$\delta(^{119}Sn)$ (p.p.m.)	ν_{as} (CO) (cm^{-1})
$Ph_3Sn(of)$	Toluene	0.03	-149.8	1560
$Np_3Sn(of)$	Toluene	0.06	51.4	1587
$Cy_3Sn(of)$	Toluene	0.06	-27.4	a
$Bu_3Sn(of)$	Toluene	0.09	70.6	1587
$Ph_2SnCl(of)$	Chloroform	0.06	-196.0	a
$Ph_2Sn(of)_2$	Chloroform	0.06	-340.7	a

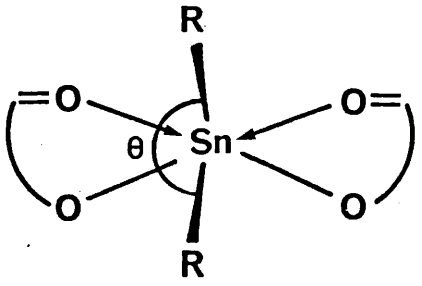
[a] Not recorded.

and, in solution, this compound shows a $\delta(^{119}Sn)$ value (Table VI) which is ca. 160 p.p.m. upfield from the 4 coordinate Ph_2SnCl_2 ($\delta(^{119}Sn)$ = -32 p.p.m.[30]). $Ph_2Sn(of)_2$ shows an even higher field chemical shift (-340.7 p.p.m.), indicative of 6 coordination (IV), the Mössbauer parameters revealing a cis-configuration of aromatic groups[24].



(IV)

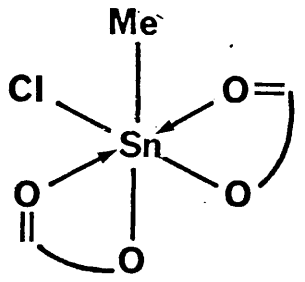
In contrast, however, the two dialkyltin complexes of 3-hydroxyflavone have ΔE_Q values consistent with distorted trans-octahedral tin atoms (V).



(V)

$Me_2Sn(ONMe.CO.Me)_2$ has been found[31] to have structure (V) and has a ΔE_Q value of 3.31 mm sec^{-1}[32]. The approximate $C\widehat{Sn}C$ bond

angle for $Me_2Sn(of)_2$ may be predicted[32] to be approximately 135^0. The ΔE_Q and δ values of $MeSnCl(of)_2$ are very similar to those of $BuSnCl(ox)_2$ (δ = 0.78, ΔE_Q = 1.65 mm sec^{-1})[33], which has an octahedral configuration[34], and therefore structure (VI) is proposed



(VI)

Of the organotin derivatives of 3-hydroxyflavone prepared, the only compounds found to be strongly fluorescent in solution were $Ph_3Sn(of)$ (excitation wavelength = 397 nm.; emission wavelength = 495 nm.) and $Ph_2SnCl(of)$ (excitation wavelength = 397 nm.; emission wavelength = 450 nm.). Aldridge[17] investigated the fluorescent properties of a number of triorganotins with 3-hydroxyflavone, and concluded that fluorescent complexes were produced only with the triphenyl- and trimethyl-tin derivatives. Attempts to prepare the trimethyltin derivative of 3-hydroxyflavone were unsuccessful, although a 1:1 mixture of trimethyltin hydroxide and 3-hydroxyflavone in toluene produced a yellow solution with a strong fluorescence emission at 510 nm (see also Table I). It is believed that the failure to isolate this complex was due to a disproportionation reaction, as has been noted for other trimethyltin complexes[28]

i.e. $2\ Me_3Sn(of) \longrightarrow Me_2Sn(of)_2 + Me_4Sn$

Evidence for this reaction was obtained from the chromatographic detection[2] of a dimethyltin species in the solid residue obtained from the preparative procedure.

The 6 coordinate R_2Sn derivatives of 3-hydroxyflavone and $MeSnCl(of)_2$ were all found to have a weak fluorescence emission at approximately 465 nm., using a 395 nm. excitation wavelength (the intensity of emission is approximately 100 times less than that of $Ph_3Sn(of)$ or $Ph_2Sn(of)_2$). Further evidence for the disproportionation of the trimethyltin complex was therefore obtained, since upon standing in solution for a few days, the 510 nm. emission was no longer present, but instead a weak emission remained with a 465 nm. maximum, suggesting the presence of $Me_2Sn(of)_2$ in solution. Similar disproportionation reactions, in solution, for the other R_3Sn derivatives were also noted by chromatographic detection[2] of R_2Sn species. The relative rates of these reactions were found to be

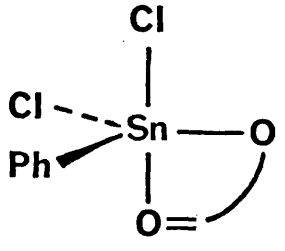
$$Me_3Sn > Bu_3Sn > Cy_3Sn \approx Np_3Sn > Ph_3Sn.$$

The instability of the triphenyltin/3-hydroxyflavone complex mentioned in Section 3.3. may therefore be ascribed to a similar disproportionation reaction.

Section 3.3. reported that the fluorescence emission of a diphenyltin species was quenched by shaking the toluene solution with saturated aqueous sodium acetate and that no fluorescence was observed when diphenyltin diacetate and 3-hydroxyflavone were mixed in solution. It has been found

that the 6 coordinate $Ph_2Sn(of)_2$ exhibits only a very weak fluorescence and so the quenching of the diphenyltin emission by sodium acetate might have been due to the formation of a similar 6 coordinate species *i.e.* $Ph_2SnOAc(of)$.

Table I reported the fluorescence emission at 450 nm. produced by mixing Bu_2SnCl_2, Me_2SnCl_2 or $PhSnCl_3$ and 3-hydroxyflavone in toluene. Although these complexes were not isolated in the solid state it is likely, since $Ph_2SnCl(of)$ has similar excitation and emission wavelengths, that the strongly fluorescent di- and mono-organotin species present in solution are $R_2SnCl(of)$ (III) and $PhSnCl_2(of)$ (VII), both of which contain pentacoordinate tin atoms.



(VII)

From this investigation it therefore appears that strong fluorescence in the organotin/3-hydroxyflavone complexes is associated with pentacoordination at tin. The fact that within the R_3SnX series only the triphenyl- and trimethyltin complexes appear to fluoresce, might indicate a relationship between fluorescence and the Lewis acidity of the tin atom.

It is therefore not unexpected that more di- and mono-organotin compounds will form fluorescent complexes with 3-hydroxyflavone, since R_2SnX_2 and $RSnX_3$ species are generally stronger Lewis acids than R_3SnX compounds.

3.6.1. Biological activity of triorganotin/3-hydroxyflavone complexes.

The triphenyl-, tributyl-, trineophyl- and tricyclohexyl-tin derivatives of 3-hydroxyflavone are undergoing a series of insecticidal tests (carried out by Dr. B. Sugavanam, ICI Plant Protection Division, Jealott's Hill Research Station) and preliminary results are given in Table VII.

The most interesting result is that the trineophyl- and tricyclohexyl-tin derivatives show no activity towards mites (tetranychus), although, in general, trineophyltin compounds, e.g. bis(trineophyltin) oxide[35], and tricyclohexyltin compounds, e.g. tricyclohexyltin hydroxide[36], exhibit very good acaricidal properties. This very low activity is possibly due to the intramolecularly coordinated carbonyl group causing a reduced tendency for the compound to attack the active sites on the protein[37]. It has been observed[38] that a similar intramolecularly coordinated compound, $Bu_3SnOCPhH.CH_2.NEt_2$, is approximately eight times less toxic orally to mice than bis(tributyltin) oxide. Hence, it is possible that the toxicity of trialkyltin compounds, R_3SnX, may be independent of the X radical only when X is a simple non-chelating group.

3.7. Experimental.

All fluorescence measurements were made on a Perkin Elmer Model 1000 fluorescence spectrophotometer. Excitation wavelengths were

Table VII: Results of insecticidal tests of triorganotin/3-hydroxyflavone complexes.

	Tetranychus		Aphid	PH	Musca	Spod.		Plutella		Diabrotica	Sitophilus	Nematode
	AD	EGG	AF		C	C	G					
$Ph_3Sn(of)$	0	9	0	0	0	0	0	0	0	0	0	0
$Bu_3Sn(of)$	0	0	0	0	9	0	0	0	0	0	0	9
$Np_3Sn(of)$	0	0	0	0	0	0	0	0	0	0	0	0
$Cy_3Sn(of)$	0	0	8	0	9	0	0	0	0	3	0	0

Compounds tested at a concentration of 250 p.p.m.

Activity score : 0 (zero activity) → 9 (high activity)

isolated by the use of discrete filters. Therefore, excitation wavelengths were determined by finding the filter which produced the maximum emission. As such, excitation wavelengths quoted are probably only accurate to ± 5 nm.. A scanning emission monochromator enabled the fluorescence emission spectrum to be recorded, and the maximum emission wavelength to be determined more accurately. A xenon discharge lamp was used as the light source. Instability in the lamp emission is compensated for by the use of the ratio-recording system, whereby the beam of exciting light is split, so that a small portion is led to a reference detector. The signal from the reference detector is then ratioed with the signal from the detector observing the sample.

^{119m}Sn Mössbauer spectra were obtained using the spectrometer system described in Section 2.8. The experimental error in the isomer shift, δ, and quadrupole splitting, ΔE_Q, parameters is ± 0.05 mm sec^{-1}.

^{119}Sn N.M.R. spectra were recorded at 25^{0}C with a JEOL FX90Q instrument, using 10 mm tubes and an internal deuterium lock on approximately 10% internal deuteriotoluene or deuteriochloroform. Spectra were recorded under nuclear Overhauser suppressed conditions (Section 1.5.1.6.). ^{119}Sn chemical shifts, $\delta(^{119}Sn)$, are quoted relative to Me_4Sn with an experimental error of ± 0.2 p.p.m.

Infrared spectra were obtained as Nujol mulls or as solutions in toluene (using KBr discs or 0.1 mm. NaCl windows) on a Grubb-Parsons Spectromaster Mark I instrument.

3-hydroxyflavone was obtained from Eastman Kodak Ltd.

With the exception of $Ph_2SnCl(of)$ and $MeSnCl(of)_2$, the complexes were prepared by an azeotropic dehydration reaction between the appropriate organotin hydroxide or oxide and 3-hydroxyflavone in refluxing toluene, using a Dean and Stark trap. Reflux times were typically 1-2 hrs. After removal of the toluene, the crude products were recrystallised from the solvents shown in Table VIII. $Me_2Sn(of)_2$ and $Ph_2Sn(of)_2$ crystallised out of the toluene solution on cooling and required no further purification. The tributylstannyl derivative of dibenzoylmethane, $Ph_3Sn(bzbz)$, was prepared similarly, m.p. 137-40^{0}C (Lit. 135-36^{0}C[28]) .

$Ph_2SnCl(of)$ crystallised on mixing equimolar quantities of Ph_2SnCl_2 and 3-hydroxyflavone at room temperature in methanol and $MeSnCl(of)_2$ was precipitated when methanolic solutions of $Bu_3Sn(of)$ (2 moles) and $MeSnCl_3$ (1 mole) were mixed and then cooled.

The analytical data, melting points and recrystallisation solvents for the new organotin/3-hydroxyflavone complexes are shown in Table VIII.

Table VIII: Analytical data for the organotin/3-hydroxyflavone complexes.

Complex	Analysis found (calcd.) (%)			M.P.	Recrystallisation solvent
	C	H	Cl	(^{0}C)	
$Ph_3Sn(of)$	67.46 (67.46)	4.25 (4.09)	-	202-5	a
$Bu_3Sn(of)$	61.51 (61.51)	6.96 (6.83)	-	54-5	a
$Cy_3Sn(of)$	65.38 (65.48)	7.10 (6.94)	-	157-60	a
$Np_3Sn(of)$	70.90 (71.52)	6.57 (6.36)	-	110-12	iso-Propanol
$Ph_2Sn(of)_2$	67.68 (67.45)	4.05 (3.90)	-	204 d	Toluene
$Bu_2Sn(of)$	64.61 (64.49)	5.19 (5.09)	-	178-80	Petroleum ether (B.P. 60-80^{0}C)
$Me_2Sn(of)_2$	61.48 (61.64)	3.96 (3.85	-	250 d	Toluene
$Ph_2Sn(of)Cl$	59.64 (59.39	3.54 (3.48)	6.41 (6.51)	192-95	Methanol
$MeSn(of)_2Cl$	57.29 (57.81)	3.40 (3.26)	5.14 (5.52)	269 d	Methanol

[a] Product obtained pure after removal of toluene.

3.8. References

1) M.D. Booth and B. Fleet, Anal. Chem., 1970, 42, 825.

2) D.J. Williams and J.W. Price, Analyst, 1964, 89, 220.

3) C.L. Luke, Anal. Chem., 1959, 31, (11), 1803.

4) G.R. Guilbault, 'Practical Fluorescence; Theory, Methods and Techniques', Marcel Dekker Inc., New York, 1973.

5) V. Patrovsky, Chem. Listy., 1953, 47, (5), 676.

6) L.B. Ginzburg and E.P. Shkrobot, Zavod. Lab., 1957, 23, (5), 527. Anal. Abs., 1957, 4, (11), 3611.

7) J.R.A. Anderson and J.L. Garnett, Anal. Chim. Acta., 1953, 8, 393.

8) J.R.A. Anderson and S.L. Lowy, Anal. Chim. Acta., 1956, 15, 246.

9) C.F. Coyle and C.E. White, Anal. Chem., 1957, 29, 1486.

10) B.K. Pal and D.E. Ryan, Anal. Chim. Acta., 1969, 48, 227.

11) T.D. Filer, Anal. Chem., 1971, 43, 1753.

12) D.G. Roux and G.C. de Bruyn, Biochem. J., 1963, 87, 435.

13) M. Nakamura and A. Murata, Mikrochim. Acta., 1980, 1, 301.

14) F. Vernon, Anal. Chim. Acta., 1974, 71, 192.

15) S.J. Blunden and A.H. Chapman, Analyst, 1978, 103, 1266.

16) P.G. Baker, D.S. Farrington and R.A. Hoodless, Analyst, 1980, 105, 282.

17) W.N. Aldridge and B.W. Street, Analyst, 1981, 106, 60.

18) C.W. Huey, Ph.D. Thesis, Univ. of Maryland, 1976.

19) T.E. Tooby, P.A. Hursey and J.J. Alabaster, Chem. Ind., 1975, 523.

20) W.N. Aldridge and J.E. Cremer, Analyst, 1957, 82, 37.

21) R.D. Barnes, A.T. Bull and R.C. Poller, Pestic. Sci., 1973, 4, 305.

22) A.H. Chapman, Personal communication.

23) 'Resistance to Continuous Salt Spray' BS. 3900 : Part 4. 1968.

24) A.G. Davies and P.J. Smith, Adv. Inorg. Chem. Radiochem., 1980, 23, 1.

25) P.G. Harrison and T.J. King, J. Chem. Soc. Dalton Trans., 1974, 2298.

26) P.G. Harrison, Inorg. Chem., 1973, 12, 1545.

27) P.J. Smith and A.P. Tupciauskas, Ann. Rept. N.M.R. Spectrosc., 1978, 8, 291.

28) G.M. Bancroft, B.W. Davies, N.C. Payne and T.K. Sham, J. Chem. Soc. Dalton Trans., 1975, 973.

29) A. Tzschach and K. Jurkschat, Paper presented at 3rd Int. Conf. Organomet. Coord. Chem. Ge, Sn, Pb, Univ. Dortmund July 1980.

30) A.G. Davies, P.G. Harrison, J.D. Kennedy, T.N. Mitchell, R.J. Puddephatt and W. McFarlane, J. Chem. Soc. (C), 1969, 1136.

31) P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc. Dalton Trans., 1975, 826.

32) P.G. Harrison, A.C.S. Advan. Chem. Ser., 1976, 157, 258.

33) A.G. Davies, L. Smith and P.J. Smith, J. Organomet. Chem., 1970, 23, 135.

34) J.D. Kennedy, W. McFarlane, P.J. Smith, R.F.M. White and L. Smith, J. Chem. Soc. Perkin II, 1973, 1785.

35) C.J. Evans, Tin and Its Uses, 1976, 110, 6.

36) C.J. Evans, Tin and Its Uses, 1970, 86, 7.

37) P.J. Smith, ITRI Publication, No.569.

38) A. Tzschach, E. Reiss, P. Helf and W. Bollman, E. Ger. Pat., 1968, 63,490.

CHAPTER 4

MULTI-NUCLEAR (^{119}Sn, ^{13}C, ^{1}H) FOURIER TRANSFORM N.M.R. STUDIES OF DI- AND TRI-BUTYLSTANNYL ETHERS OF CARBOHYDRATES.

4.1. Introduction.

The organotin derivatives of 3-hydroxyflavone, described in Section 3.6., represent a special class of organotin alkoxides in that they are hydrolytically stable. Triorganotin alkoxides, R_3SnOR', which may be prepared[1] by the reaction between a bis(triorganotin) oxide or triorganotin hydroxide with the appropriate alcohol or dialkyl carbonate,

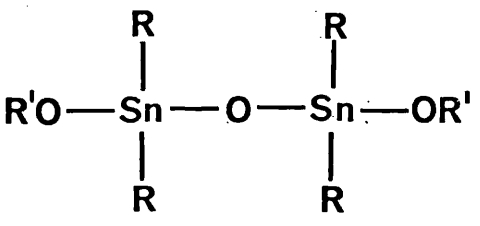
$$(R_3Sn)_2O + 2R'OH \longrightarrow R_3SnOR' + H_2O$$

$$R_3SnOH + R'OH \longrightarrow R_3SnOR' + H_2O$$

$$(R_3Sn)_2O + (R'O)_2CO \longrightarrow 2R_3SnOR' + CO_2$$

are usually very readily hydrolysed in air.

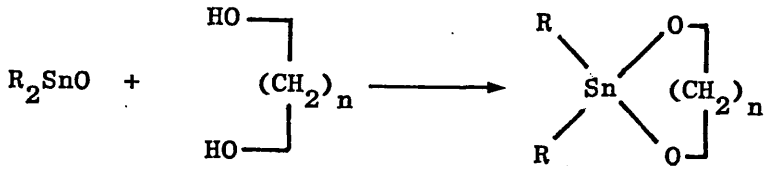
Similar reactions with dialkyltin oxides usually produce[1] compounds of the type



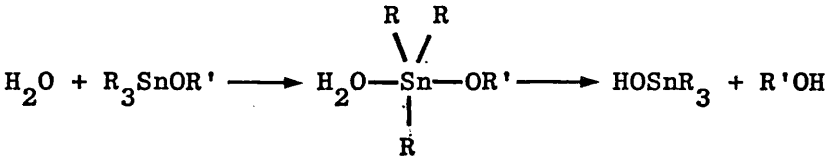
Therefore, dialkyltin dialkoxides are produced by reaction of a dialkyltin dihalide with the appropriate sodium alkoxide[1].

$$R_2SnX_2 + 2NaOR' \longrightarrow R_2Sn(OR')_2 + 2NaCl$$

However, reaction of a dialkyltin oxide with 1,2-, 1,3-, or 1,4- diols produces a cyclic dialkyltin alkoxide



The high reactivity of acyclic organotin alkoxides is possibly due to the ability of the tin atom to form a five-coordinate intermediate species: e.g. for hydrolysis.



In the above equations R' may be a carbohydrate residue and, thus, the di- and tri-alkylstannyl ethers of carbohydrates may be prepared by such methods. These compounds are also generally very reactive, and, since Moffatt and his colleagues[2,3] first prepared such compounds, the di- and tri-butylstannyl ethers have found wide use in carbohydrate chemistry, particularly as reaction intermediates[4,5]. Smith and Crowe[6,7], prepared several tributylstannyl-carbohydrate derivatives for an investigation into the possibility of the wood-preservative, bis(tri-n-butyltin)

oxide, bonding to wood cellulose. Inorganic tin salts, e.g. $SnCl_2$, have also been suggested as catalysts for the mono-methylation of the cis-diol system in nucleosides[8] and carbohydrates[9] by diazomethane. There are, however, few structural studies[6,7,10,11] of these tin-carbohydrate derivatives. The object of this work was, therefore, to see if further structural information could be extracted by a multi-nuclear Fourier transform N.M.R. investigation.

The compounds studied were the tributylstannyl ethers of 2,3,4,6-tetra-O-methyl-D-glucose, 1,2,3,4-diisopropylidene-α-D-galactopyranoside, methyl 2,3-di-O-methyl-α-D-glucopyranoside and methyl 4,6-O-benzylidene-α-D-glucopyranoside, and the dibutylstannyl ether of the last sugar.

4.2. Results and discussion.

4.2.1. ^{119}Sn chemical shifts.

The ^{119}Sn chemical shifts, $\delta\ ^{119}Sn$, for the compounds studied are recorded in Table I. The O-tributylstannyl derivatives and bis(tri-n-butyltin) oxide all showed ^{119}Sn N.M.R. resonances which were 70-100 p.p.m. downfield from Me_4Sn. These values indicate[12] that the geometry at the tin atom is tetrahedral, since it is well established that inter- or intra-molecular coordination to tin leads to significant shifts to higher field[12]. For example, tributyltin-8-hydroxyquinolate which contains[13] an intramolecularly chelated, five coordinate tin atom

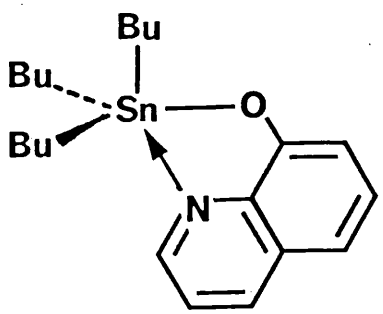
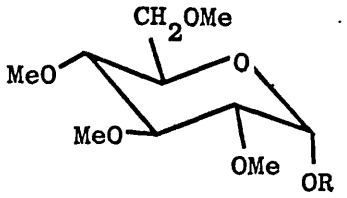
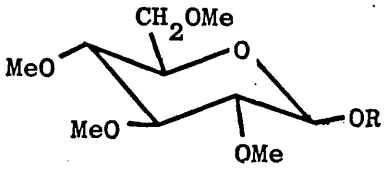
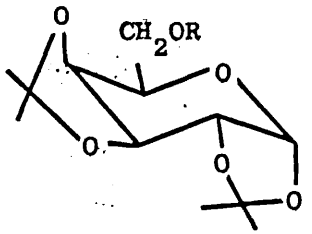
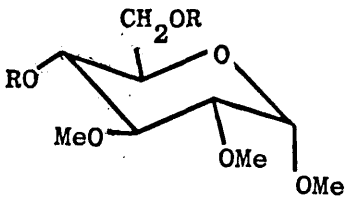


TABLE I: ^{119}Sn chemical shifts[a] and coupling constants[b] in toluene solution for the organotin - carbohydrate derivatives

Compound (R = $SnBu_3$)		Approximate concentration (M)	$\delta\ ^{119}Sn$	$^2J(^{119}Sn\text{-}O\text{-}^{13}C)$	$^3J(^{119}Sn\text{-}O\text{-}C\text{-}^{13}C)$
	(1a)	0.2	99.0[c]	24	16
	(1b)	0.9	86.4[c]	23	13
	(2)	1.1	98.7	46	29[d]
	(3)	1.2	92.8[e] 98.6[e]	f	f

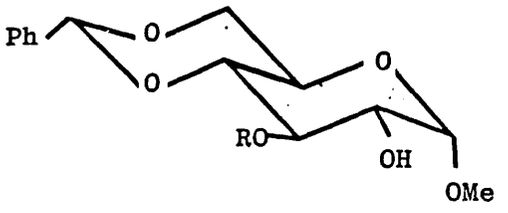
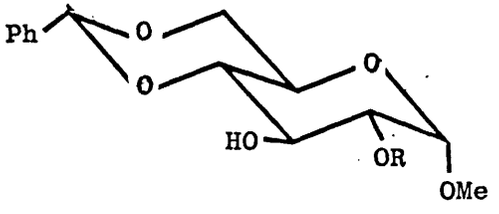
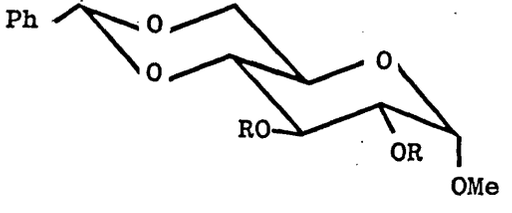
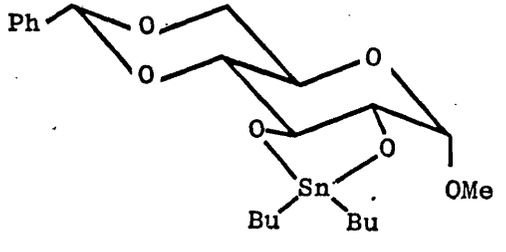
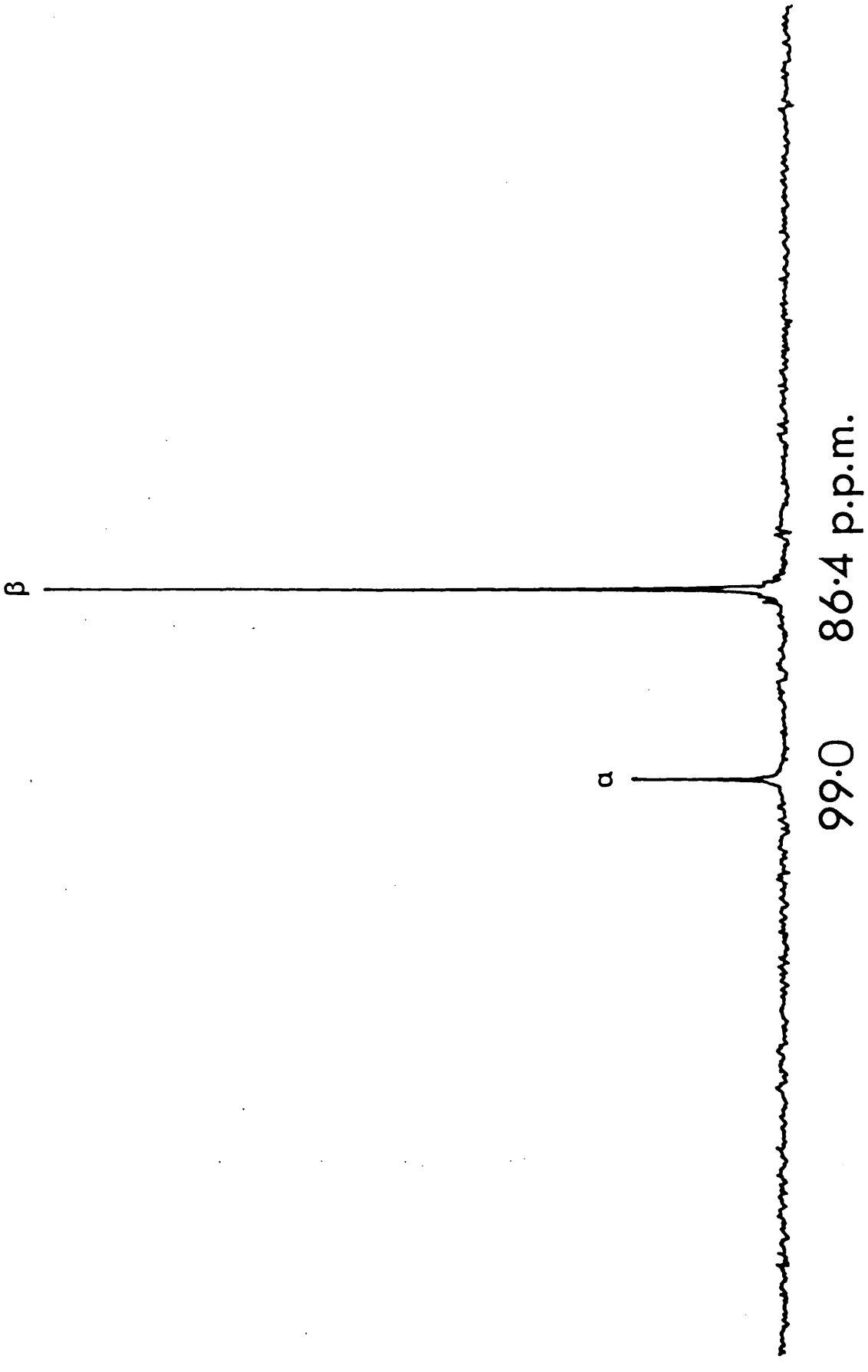
	(4)	0.2	101.8[g]	29	~ 18 (C-4) ~ 20 (C-2
	(5)	0.05	87.3[g]	h	h
	(6)	0.4	77.5 (C-2)[g] 91.2 (C-3)[g]	29 (C-2) 28 (C-3)	19 (C-1) 22 (C-2) 16 (C-3) < 18 (C-4)[i]
	(7)	0.6	-131.6[j]	12[e,k] < 10[e,i,k]	34 (C-4)[k] 20 (C-1)[k]
$Bu_3SnOSnBu_3$	(8)	50% v/v	82.8[l]	f	f

TABLE I: (Cont'd...3).

[a] In p.p.m. downfield from Me_4Sn; error in δ (^{119}Sn) is ± 0.2 p.p.m. [b] In Hz; estimated error is ± 1 Hz. [c] Recorded as mixture of two anomers. [d] A possible alternative assignment, with this as a 4-bond coupling to C-4, was considered unlikely. [e] Assignment uncertain. [f] Not recorded. [g] In mixture of (4), (5) and (6). [h] No satellites were observable, due to low concentration. [i] Not resolved. [j] Ref. 10 reports -132.0 p.p.m. converted to Me_4Sn. [k] Note that these couplings involved two different bonding pathways. [l] Ref. 12 reports 77.8 p.p.m.—84.5 p.p.m.

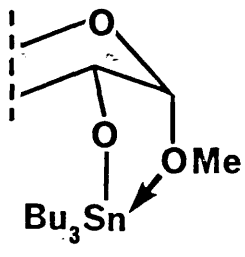
FIGURE I

^{119}Sn F.T.N.M.R. spectrum of the product of the reaction between bis(tri-n-butyltin) oxide and 2,3,4,6-tetra-O-methyl-D-glucose in toluene, at 37.08 MHz, recorded using 40 pulses.


β
α
99·0
86·4 p.p.m.

has a ^{119}Sn chemical shift of 29.0 p.p.m.,[12] which is approximately 50 p.p.m. to high field of four coordinate species.

Ogawa and Matsui[14] studied the acylation of trialkyltin derivatives of several methyl glucosides and concluded that the stereochemistry at the anomeric carbon was of importance in obtaining substitution at C-2. This they rationalised in terms of the ability of the α- anomer to form a more stable organotin intermediate through intramolecular coordination from the methoxy group to the tin atom.



The present results, however, argue against this suggestion because a similar structure to that shown above would be encountered in compounds (5) and (6), yet the ^{119}Sn chemical shifts clearly demonstrate that the tin atom has a coordination of four.

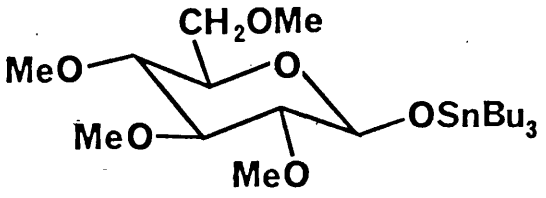
A typical ^{119}Sn spectrum, obtained for the product of the reaction of bis(tri-n-butyltin) oxide with 2,3,4,6-tetra-O-methyl-D-glucose in toluene solution is shown in Figure I. This spectrum shows two ^{119}Sn resonances, separated by 12.6 p.p.m.. The position and magnitude of the anomeric doublet in the ^{1}H N.M.R. spectrum of carbohydrates is indicative of the anomeric form, whether α or β, of the sugar. Thus, the more intense peak in the ^{119}Sn spectrum was identified by

inspection of the anomeric doublets in the ^{1}H spectrum, where the more intense doublet (δ4.77 p.p.m., J ~ 6 Hz.) was assigned to the β anomer (1b) and the less intense (δ5.35 p.p.m., J ~ 4 Hz.) to the α anomer (1a). The proportions of the anomeric species deduced from the ^{119}Sn peak heights were 21% for (1a) and 79% for (1b), and since there was no dependence of the relative concentration of the two species on temperature (between 25 and 100^{0}C) it may be said that they were not in chemical equilibrium. ^{1}H N.M.R. spectra of the parent-sugar, 2,3,4,6 tetra-O-methyl-D-glucose, in toluene solution, were recorded at different temperatures, and revealed, again by inspection of the anomeric doublets, that the percentage of each anomer was as follows:

Temp. (^{0}C)	α (%)	β (%)
18	64.9	35.1
67	58.9	41.1
90	55.8	44.2

Thus, the α- anomer can be seen to be the preferred conformation of the sugar over the given temperature range. This is in contrast to the preponderence of the β- anomeric form of its tributylstannyl ether.

In the β- conformation the bulky tributylstannyloxy group is occupying an equatorial position, and so steric interactions are reduced



It, therefore, appears that bis(tri-n-butyltin) oxide reacts preferentially with the β-anomer and that the sugar is undergoing anomerisation in solution.

It was hoped that the ^{119}Sn chemical shift would be indicative of the position of substitution on the carbohydrate ring. Unfortunately no clear pattern emerges from the few compounds studied. However, compounds (2) and (3) both have a tin-substituent at C-6 and ^{119}Sn resonances at 98.7 and 98.6 p.p.m. respectively. This might be indicative of a more general consistency of shift at C-6. From the ^{119}Sn chemical shifts of compounds (1a) and (1b) it also appears that the change in the position of the resonance for the two anomeric species is comparable in magnitude to that obtained on changing the site of substitution in compounds (3) and (6).

The dibutylstannylene derivative of methyl 4,6-O-benzylidene-α-D-glucopyranoside (7) has been shown[10] by X-ray crystallography in the solid state, and by ^{119}Sn F.T.N.M.R. in solution to exist as a dimer having the structure illustrated in Figure II. No evidence was found for the alternative form of the dimeric structure of (7) involving the donation of electrons from O-2 to tin[10]. This dimeric structure contains a five coordinate tin atom, and the ^{119}Sn chemical shift, -131.6 p.p.m., may be compared with that of $Bu_2Sn(OMe)_2$ (-165 p.p.m.)[12], which has a similar oxygen-bridged structure[15,16].

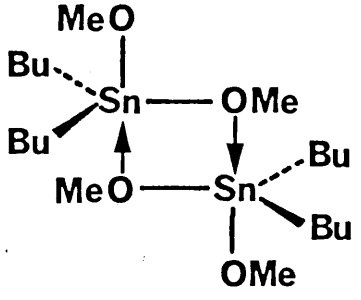
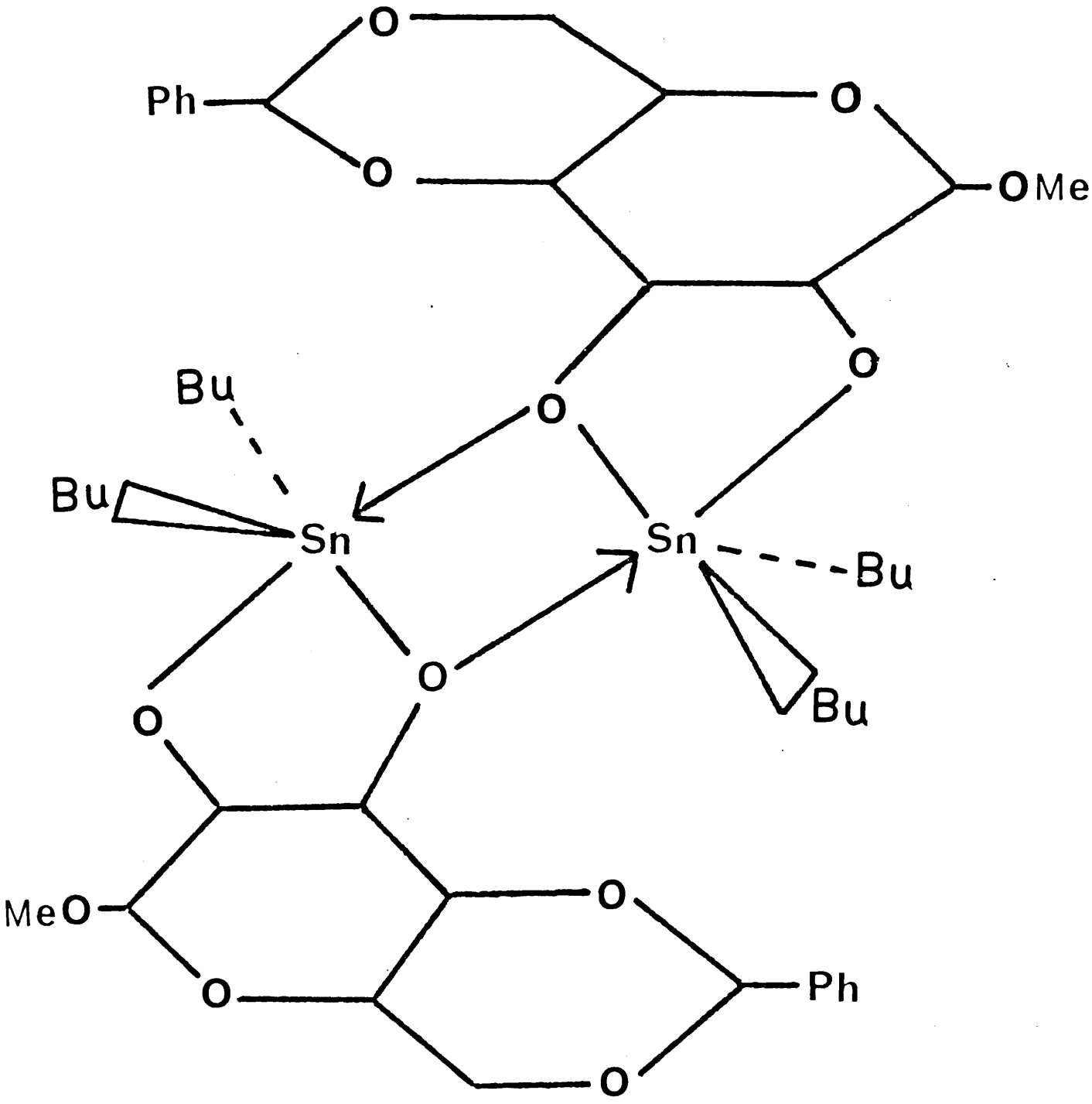
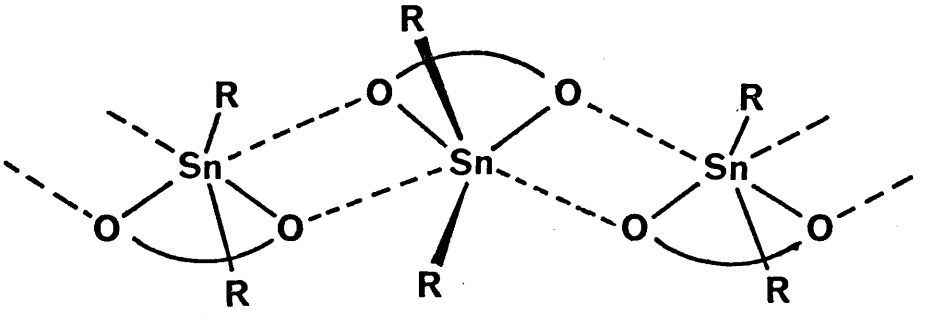


FIGURE II

The dimeric structure of the dibutylstannylene derivative of methyl 4,6-O-benzylidene-α-D-glucopyranoside[10].


O
Ph
O
O
OMe
O
O
Bu
O
Bu
Sn
Sn
Bu
Bu
O
O
MeO
O
O
Ph
O

It is of interest to compare these shifts with that of $Bu_2\overline{Sn(OCH_2CH_2CH_2O)}$ (-228 p.p.m.)[12] which has been shown crystallographically to exist as a polymer in the solid state with six coordinate tin[17].



This increase in coordination number is reflected in the slightly higher value of δ ^{119}Sn .

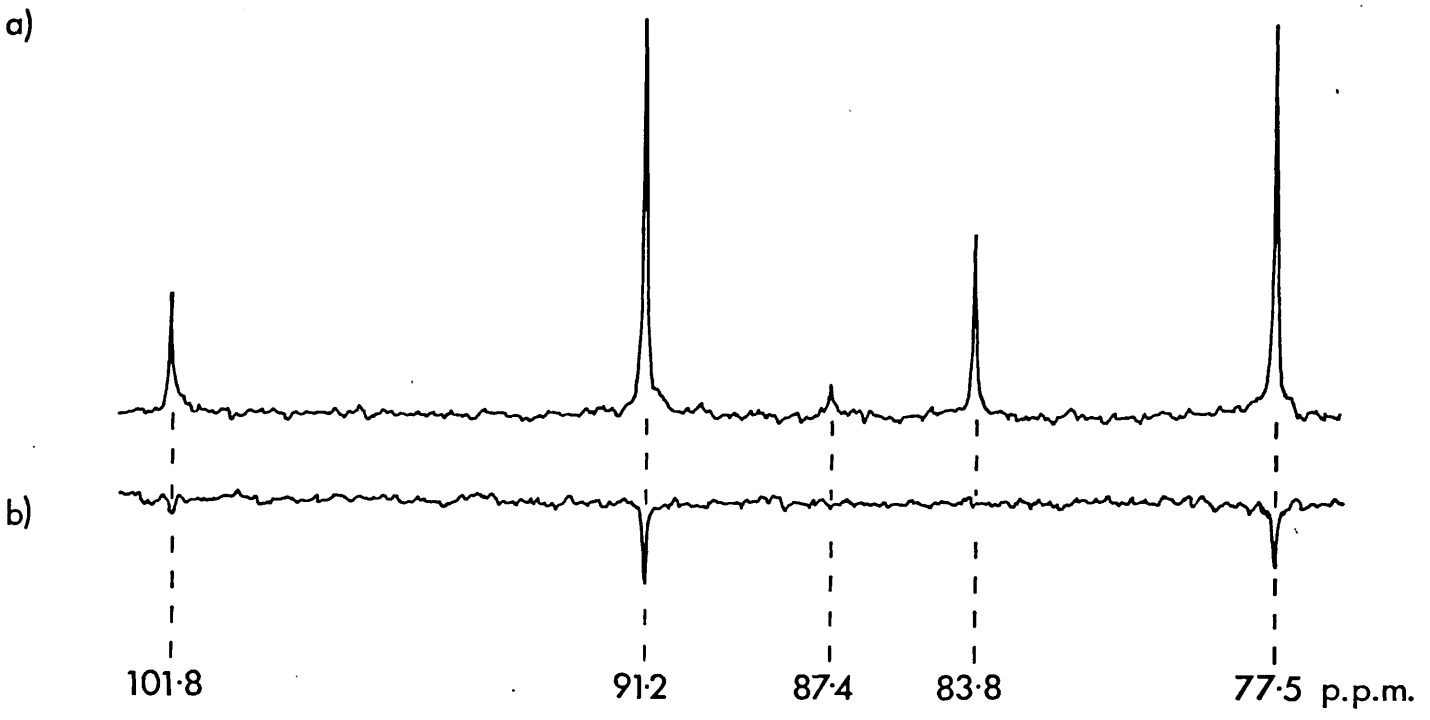
4.2.2. Order of reactivity of the hydroxyl groups in methyl 4,6-O-benzylidene-α-D-glucopyranoside with bis(tri-n-butyltin) oxide.

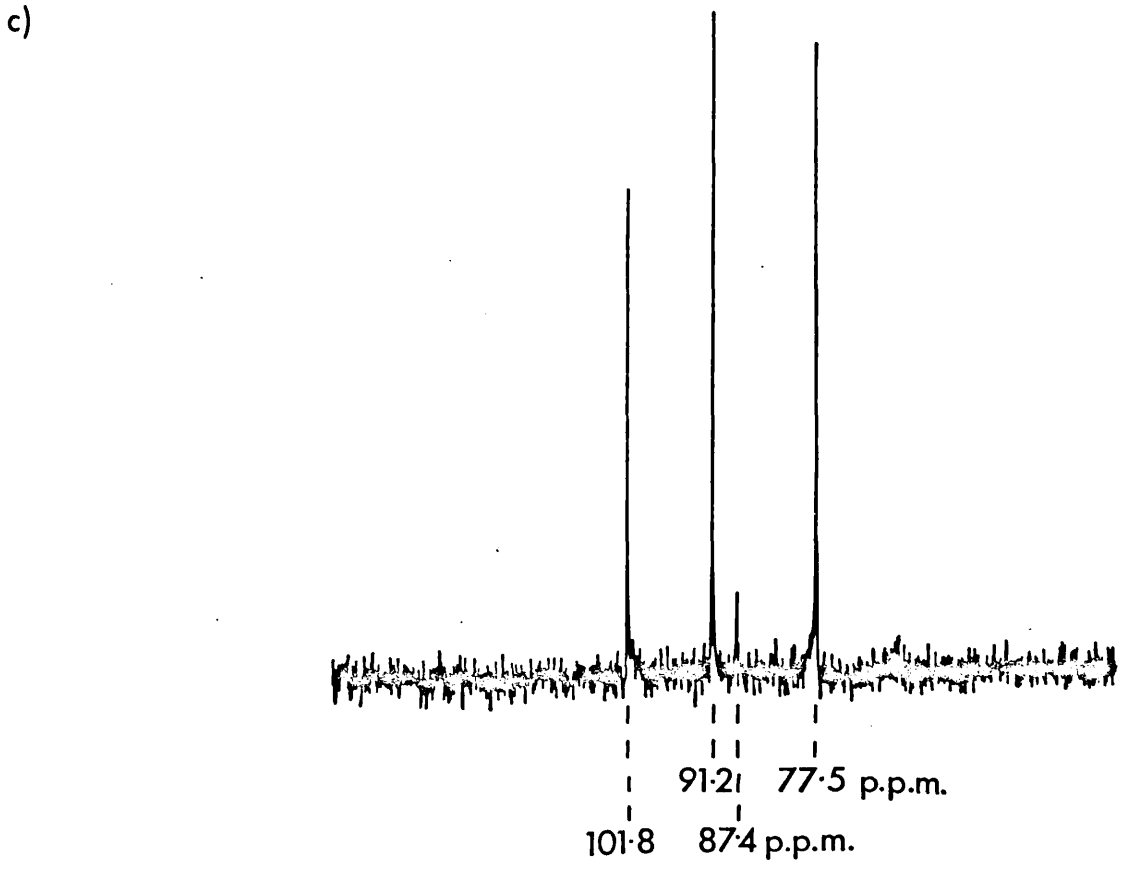
The reaction of methyl 4,6-O-benzylidene-α-D-glucopyranoside with bis(tri-n-butyltin) oxide had not been studied previously and was found to follow a rather complicated pattern. After refluxing equimolar amounts of the reactants in toluene for 4 hours a ^{119}Sn spectrum, was obtained which showed five resonances, Figure IIIa. A spectrum recorded after refluxing the solution for 24 hours showed the same two major resonances at 77.5 and 91.2 p.p.m., which were attributed to the 2,3-bis(tributylstannyl) ether (6). The two peaks at 83.8 and 101.8 p.p.m. were still

FIGURE III

^{119}Sn F.T.N.M.R. spectra of the products of the reaction of bis(tri-n-butyltin) oxide with methyl 4,6-O-benzylidene-α-D-glucopyranoside in toluene:

a) stoichiometric amounts boiled under reflux for 4 hours;
b) as for (a), but with N.O.E.;
c) solution (a) boiled for a further 12 hours with excess of carbohydrate.


a)
b)
101·8
91·2
87·4
83·8
77·5 p.p.m.


c)
91·2
77·5 p.p.m.
101·8
87·4 p.p.m.

present, but at one third their previous intensity, and the small peak at 87.4 p.p.m. was no longer visible.

Addition of excess sugar to the solution that gave the spectrum shown in Figure IIIa, followed by refluxing for a further 12 hours, resulted in the spectrum shown in Figure IIIc. Comparison with Figure IIIa shows that the peak at 83.8 p.p.m. has disappeared, whereas the resonances at 87.4 and 101.8 p.p.m. both increased in intensity. It, thus, appears that the peak at 83.8 p.p.m. was due to unreacted bis(tri-n-butyltin) oxide (8), while the resonances that increased in intensity correspond to the mono-O-tributylstannylated sugars, (4) and (5).

The ^{13}C spectrum of methyl 4,6-O-benzylidene-α-D-glucopyranoside in deuteriochloroform has been assigned previously[18] and was found to match the data for the present toluene solution given in Table II. ^{13}C spectra were also recorded for the refluxed solutions described above. By comparison of these spectra with that of the parent-sugar and also with the corresponding ^{119}Sn N.M.R. spectra, it was possible to assign the ^{13}C peaks to the mono- and di- substituted derivatives, see Table II and Figure IV. The observance of tin satellites (discussed in Section 4.2.4) on some of the ^{13}C peaks was an extremely valuable aid to assignment. In Figure IIIa the ^{119}Sn peak at 101.8 p.p.m. was attributed to the preponderent mono-substituted derivative, the 3-tributylstannyl ether (4) and the peak at 87.4 p.p.m. was assigned to the 2-substituted compound (5). The peaks at 77.5 and 91.2 p.p.m. were assigned to the groups at the 2- and 3- positions respectively, of the disubstituted derivative (6).

TABLE II: ^{13}C chemical shifts[a] in toluene for methyl 4,6-O-benzylidene-α-D-glucopyranoside and its tributylstannyl derivatives (4), (5) and (6).

COMPOUND	C-1	C-2	C-3	C-4	C-5	C-6	C-7	OMe
PARENT SUGAR	100.4	73.5	72.1	81.5	62.9	69.1	101.9	55.0
(4)	101.0	74.1	75.4	84.1	63.2	69.2	102.6	54.9
(5)	b	76.3	72.5	82.4	b	b	b	54.9[c]
(6)	103.0	78.8	75.4	84.9	62.9	69.4	103.4	54.9

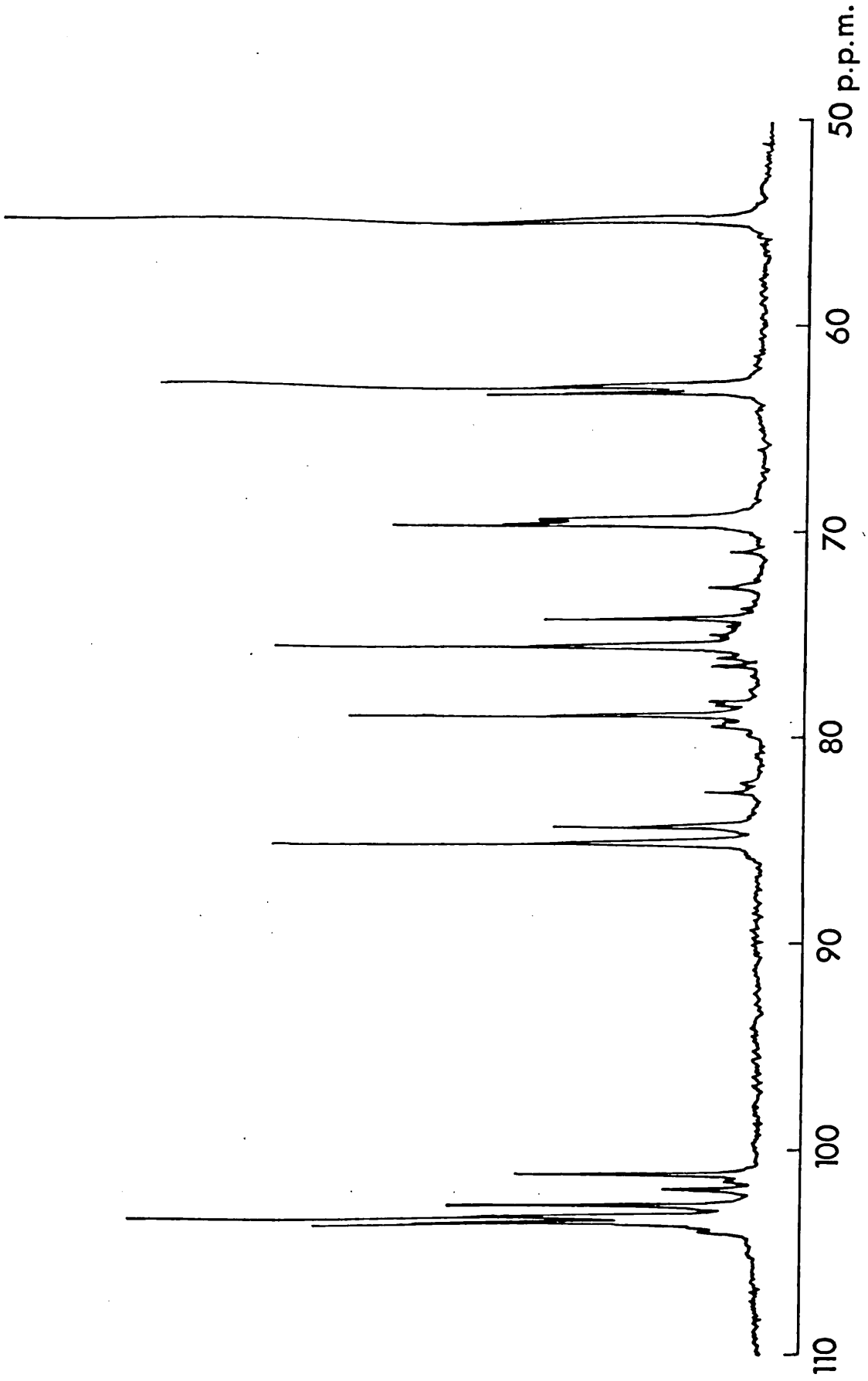
[a] In p.p.m. downfield from T.M.S., measured from the methyl resonance of toluene, taken as 21.3 p.p.m.; chemical shifts of (4), (5) and (6) were recorded as a mixture.

[b] Not assignable.

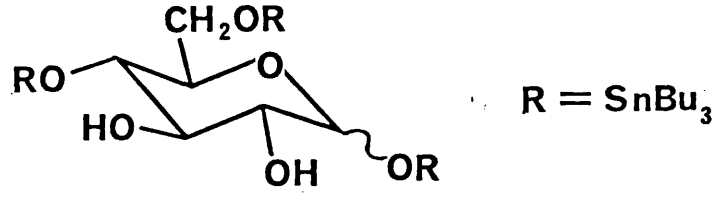
[c] Presumed coincident with the methoxy resonances of (4) and (6).

FIGURE IV

^{13}C F.T.N.M.R. spectrum showing the ring carbon region, of the products of the reaction of bis(tri-n-butyltin)oxide with methyl 4,6-O-benzylidene-α-D-glucopyranoside in toluene (reflux, 4 hours) recorded at 25.0 MHz., using 1000 pulses.


50 p.p.m.
60
70
80
90
100
110

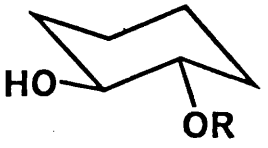
The above results indicate that the 3- position is much more reactive to initial substitution than the 2- position. This was confirmed by a ^{13}C spectrum run after 30 mins. refluxing, which showed that the mono-substituted derivative (4) and the di-substituted derivative (6) were present in comparable amounts, but the 2-O-tributylstannyl ether (5) was very much less evident. It seems that substitution of (4) at the 2- position to form (6) occurs with an ease nearer to that for the initial substitution to form (4), in contrast to the relative difficulty of initial substitution at the 2- position. The reduced susceptibility of HO-2 to tributylstannylation may possibly be due to the formation of an intramolecular hydrogen-bond with the axial MeO-1. This difference in reactivity for tributylstannylation has been noted previously for other sugars [6,7,14]. Smith and Crowe,[6,7] in a study of the reactions of bis(tri-n-butyltin)oxide with D-glucose and various substituted glucopyranosides and galactopyranosides, found the 1,4 and 6 - OH groups were most susceptible to attack.



The reaction of bis(tri-n-butyltin)oxide with D-glucose was briefly investigated by ^{119}Sn F.T.N.M.R. spectroscopy. A spectrum recorded for the products of the reaction, showed

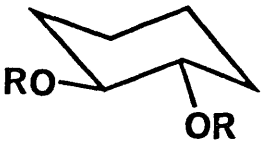
three main peaks (δ ^{119}Sn = 95.8, 85.6 and 85.1 p.p.m.), but also contained many other resonances ranging from 57 - 137 p.p.m.. It therefore seems that the three main peaks were possibly due to the 1,4,6 tributylstannyl ether, confirming the findings of Smith and Crowe,[6,7] and that the other peaks were due to various combinations of mono- and di-substituted compounds. Since D-glucose can exist in both the α- and β- anomeric form, peaks should also be present due to both anomers. Owing to the complexity of the ^{119}Sn spectrum recorded for this reaction, the system was not investigated further.

Another compound containing two OH groups on adjacent carbon atoms is trans-1,2-cyclohexanediol, and, although this is not a carbohydrate, its reaction with bis(tri-n-butyltin)oxide was also briefly investigated. A ^{119}Sn spectrum recorded for a toluene solution, in which equimolar amounts of the two reactants had been refluxed, showed two peaks at 77.8 and 90.8 p.p.m. of which the former was the more intense. The spectrum of a solution refluxed with a 2:1 molar ratio of cyclohexanediol to bis(tri-n-butyltin) oxide produced the same two peaks but, in this case, that at 90.8 p.p.m. was the more intense. The resonance at 90.8 p.p.m. was, therefore, ascribed to the mono-substituted tributylstannyl ether



$R = Bu_3Sn$

and that at 77.8 p.p.m. to the di-substituted compound.



$R = Bu_3Sn$

Since the di-substituted species was clearly in evidence when the reflux was carried out with an excess of the diol, it was also concluded that the ease of substitution to form the mono-tributylstannyl ether is comparable to that of second tributylstannylation to form the di-substituted compound.

4.2.3. Effect of substituents on ^{13}C resonances.

Since the ^{13}C spectrum of methyl 4,6-O-benzylidene-α-D-glucopyranoside has been assigned,[18] Table II, it was possible to study the effect of tributylstannylation on the ^{13}C chemical shifts. As expected, the largest effects were at the site of substitution, where a 3.3 p.p.m. shift occurred for the C-3 derivative (4), 2.8 p.p.m. for the C-2 derivative (5), and 5.3 and 3.3 p.p.m. for the diether (6) at C-3 and C-2 respectively, Table III. Significant effects were also noted at the carbon adjacent to the site of substitution, although not necessarily on both adjacent carbons. For instance, in compound (4), a shift of 2.6 p.p.m. is seen at C-4, but only 0.6 p.p.m. at C-1. With compound (5), an insignificant shift of 0.4 p.p.m. occurs at C-3, but the effect at C-1 could not be determined, due to the peak not being assignable. For the di-substituted species (6),

shifts of 2.6 and 3.4 p.p.m. were found for C-1 and C-4 respectively. The data for these compounds may be rationalised in two ways. Starting with the C-3 tributylstannyl ether (4) and substituting at C-2 gives rise to shifts of 2.0, 4.7 and 0.0 p.p.m. at C-1, C-2 and C-3 respectively. Alternatively, starting with the C-2 tributylstannyl ether (5) and substituting at C-3, effects of 2.9 and 2.5 p.p.m. are experienced at C-3 and C-4, but, in this case, a shift of 2.5 p.p.m. also occurs at C-2, which is already tributylstannylated.

The ^{13}C chemical shifts determined for the dibutylstannylene derivative of methyl 4,6-O-benzylidene-α-D-glucopyranoside (7) are given below.

C-1	C-2/3	C-2/3	C-4	C-5	C-6	C-7	OMe
105.4	79.7	74.3	85.3	65.6	71.1	105.7	56.4 p.p.m.

The uncertainty in the assignment of the ^{13}C signals for C-2 and C-3 leads to two possible values for the substituent effects. However, the shift changes, with respect to the parent sugar on dibutylstannylation are as follows:

C-1	C-2	C-3	C-4	C-5	C-6	C-7	OMe
5.0	0.8(6.1)	7.6(2.3)	4.0	2.8	1.9	3.9	1.4 p.p.m.

The figures in brackets denote the alternative assignment.

It can be seen that, in general, these effects are larger than those for compounds (4)-(6). The dimeric structure, Figure II, of the dibutylstannylene derivative, involves electron donation from O-3 → Sn. It would be expected that this might lead to a deshielding of C-3, resulting in a significant shift to low field.

TABLE III: ^{13}C substituent effects[a] on tributylstannylation of methyl 4,6-O-benzylidene-α-D-glucopyranoside

COMPOUND	C-1	C-2	C-3	C-4	C-5	C-6	C-7	OMe
(4)	0.6	0.6	3.3	2.6	0.4	0.1	0.7	-0.1
(5)	b	2.8	0.4	0.9	b	b	b	-0.1
(6)	2.6	5.3	3.3	3.4	0.0	0.3	1.5	-0.1

[a] Substituent effect in p.p.m. = δ (tributylstannyl derivative) - δ (parent sugar).

[b] Peak not assigned.

If this is the case, then the 7.6 p.p.m. substituent effect is the preferred assignment for this carbon resonance.

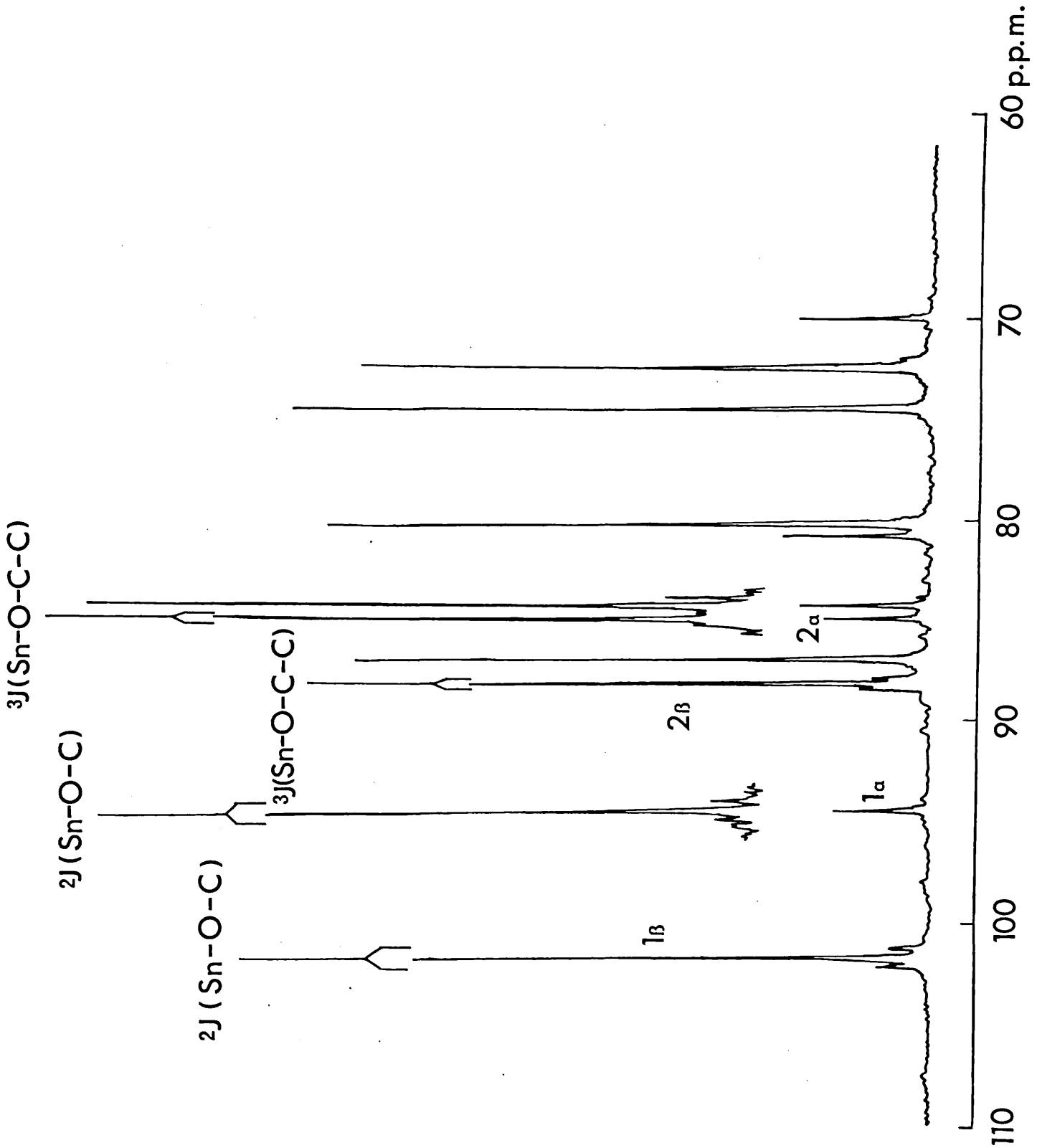
The relative changes in chemical shift upon di- and tributylstannylation of methyl 4,6-O-benzylidene-α-D-glucopyranoside cannot be explained. For instance, no reason can be seen why substitution should have an effect upon one adjacent carbon but not the other. Obviously, many more such measurements will need to be made before these substituent effects are fully understood.

4.2.4. Tin-carbon coupling constants.

An interesting feature of the ^{1}H decoupled ^{13}C spectra of the organotin-carbohydrate derivatives is the appearance of satellites due to coupling with the ^{119}Sn nucleus, Table I. An example of a ^{13}C spectrum in which coupling from the ring carbon atoms to tin is visible is shown in Figure V. The satellites on C-1 arising from $^{2}J(^{119}Sn\text{-}O\text{-}^{13}C)$, and on C-2, arising from $^{3}J(^{119}Sn\text{-}O\text{-}C\text{-}^{13}C)$, are clearly visible for both anomers and the magnitude of ^{3}J is less than that of ^{2}J. No $J(^{119}Sn\text{-}O\text{-}^{13}C)$ couplings have previously been observed, although Davies et al[19] observed $^{3}J(^{119}Sn\text{-}O\text{-}C\text{-}^{1}H)$ couplings in tributyltin alkoxides, Bu_3SnOR, only where R is very bulky. This effect was ascribed to a low rate of exchange of the alkoxy moieties in solution between different tin sites, and a similar situation would be expected to occur in the present case where R is a large carbohydrate. Since no previous $J(^{119}Sn\text{-}O\text{-}^{13}C)$ measurements have been reported, it is not possible to compare the results obtained to see if the magnitude is typical of such couplings. However, measurements of the type $J(^{119}Sn\text{-}C\text{-}^{13}C)$ have been made[20] and these are of the same order as $J(^{119}Sn\text{-}O\text{-}^{13}C)$.

FIGURE V

^{13}C F.T.N.M.R. spectrum showing the ring carbon region of the product of the reaction of bis(tri-n-butyltin) oxide with 2,3,4,6-tetra-O-methyl-D-glucose in toluene, recorded at 25.0MHz., using 1000 pulses.

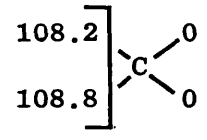

3J(Sn-O-C-C)
2J(Sn-O-C)
3J(Sn-O-C-C)
2J(Sn-O-C)
1β
2β
1α
2α
110
100
90
80
70
60 p.p.m.

The dibutylstannylene derivative of methyl 4,6-O-benzylidene-α-D-glucopyranoside (7) presents problems in the assignment of the couplings, because the carbon atoms at the position of substitution each have both two- and three- bond pathways to the tin atom. In such cases, the observed couplings will be the algebraic sum of the two contributions[21]. The resonances which showed couplings of 34- and 20-Hz., Table I, were assigned to C-4 and C-1 respectively by consideration of the ^{13}C chemical shifts. The lowest field peak was assigned to C-1 on account of the close proximity of two oxygen atoms, and the C-4 resonance was located by comparison with a previously assigned spectrum[18] of the parent-sugar. Unfortunately similar considerations could not definitely ascribe the 12 Hz. coupling to either C-2 or C-3. A further set of satellites should have been observed but were presumably unresolved due to the splitting being less than 10 Hz.. The couplings to C-2 and C-3 (12 and < 10 Hz.) are low compared to normal two-bond values and, presumably, result from algebraic addition of two- and three- bond contributions that are opposite in sign. In addition, the butyl region of the ^{13}C spectrum of the dibutylstannylene derivative (7) revealed that the two butyl groups attached to the tin atom are not equivalent. Two distinct sets of one bond Sn-C coupling were seen and were found to be the same for both butyl groups, 614 and 588 Hz. for ^{119}Sn and ^{117}Sn respectively. The reason for the non-equivalence of the two groups becomes apparent if a 'stick and ball' model of the dimeric structure, Figure II, is made, for it can be seen that one of the butyl groups attached to each tin atom is sterically restricted, whilst the other is reasonably unhindered.

Tin-carbon couplings provide an extremely valuable aid to the assignment of individual resonances in the ^{13}C spectrum. As such, the ^{13}C chemical shifts of compounds (1a), (1b) and (2) are reported in Table IV and assignments where possible, based on tin-carbon couplings, are given in brackets.

TABLE IV: ^{13}C N.M.R. chemical shifts (in p.p.m. relative to TMS) of compounds (1a), (1b) and (2).

(1a)	(1b)	(2)
94.4 (C-1)	101.8 (C-1)	96.8 (C-1)[b]
84.9 (C-2)	87.9 (C-2	71.1
84.2	86.2	71.4
80.8	80.2	71.4
74.5[a]	74.5	70.4 (C-5)
70.0	72.4	65.2 (C-6)
60.2	60.5	108.2
59.9[a] OMe	59.9 OMe	108.8
58.9	59.7	
58.2	58.6	



[a] assumed coincident with 1b.

[b] C-1 is found at the lowest field due to the close proximity of two O atoms.

4.2.5. Spin-lattice relaxation times and nuclear Overhauser effects.

The spin-lattice relaxation times, T_1, and nuclear Overhauser factors, η, for the compounds studied are reported in Table V. The measurements were made upon solutions whose concentrations are given in Table I.

It can be seen from Table V that the values of T_1 fall within the range of approximately 2-6 secs., and so are similar to previous measurements by other workers[22-27] (see also Section 1.5.1.7.). The nuclear Overhauser factor, η, was discussed in Section 1.5.1.6. and was said to arise from the dipolar contribution to T_1. The values of η recorded, Table V, range from -0.6 to -1.2 (49 - 92% dipolar relaxation) and are in agreement with the work of Frangou[27], who found that dipole-dipole relaxation was a much more important mechanism for tin than had been previously realised. Of the other possible T_1 relaxation processes (Section 1.5.1.4.), scalar coupling and nuclear quadrupole relaxation cannot apply to the compounds studied. The contribution from chemical shift anisotropy (CSA) is assumed to be negligible. Frangou[27] reported identical ^{119}Sn T_1 and η values at 22 and 37 MHz except in one case where chemical exchange was present. In fact the CSA mechanism has never been shown to be relevant for tin. Therefore the non-dipolar contribution to T_1 may be taken as arising from spin-rotation.

In general, it can be seen from Table V that as the molecular weight of the molecule increases so too does η, thus, indicating that the dipolar mechanism is becoming more important. This is also illustrated by a similar increase in the dipolar relaxation rate, R_1^{DD}, and corresponding decrease in the spin-rotation rate,

TABLE V: Spin-lattice relaxation times and nuclear Overhauser factors.

Compound	M.W.	T_1 (secs.)	R_1 (secs.$^{-1}$)	η	% D-D	R_1^{DD} (secs.$^{-1}$)	R_1^{SR} (secs.$^{-1}$)	τ_c (psecs.)
1a	525	6.3	0.159	- 0.78	58.5	0.093	0.066	62
1b	525	6.15	0.163	- 0.84	62.5	0.102	0.061	68
2	548	5.58	0.179	- 0.97	72.6	0.129	0.05	86
4	571	3.19	0.314	- 1.17	87.8	0.275	0.038	183
6	860	(C-2) 2.80	0.357	- 1.18	85.5	0.316	0.041	211
		(C-3) 2.32	0.431	- 1.23	91.7	0.396	0.036	263
8	596	6.56	0.152	- 0.66	48.9	0.075	0.078	50

TABLE V: cont'd...2.

Abbreviations:

M.W. = Molecular weight

T_1 = Spin-lattice relaxation time

R_1 = Spin-lattice relaxation rate = $\frac{1}{T_1}$

η = Nuclear Overhauser factor, $\eta max.$ = - 1.34

% D-D = Percentage of dipole dipole relaxation = $\frac{\eta}{\eta max} \times 100$

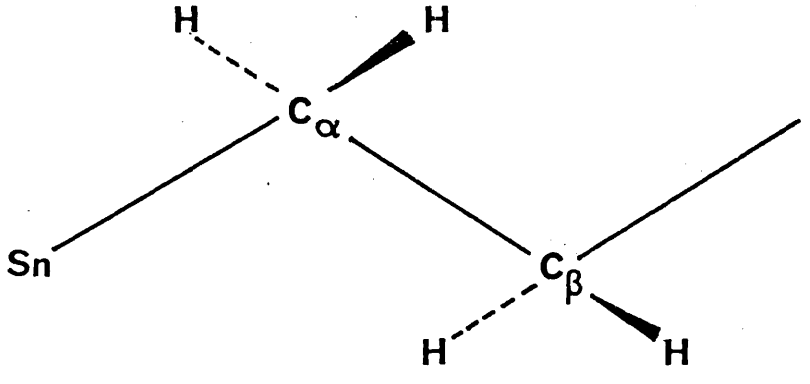
R_1^{DD} = Dipole-dipole relaxation rate = $R_1 \times \frac{\eta}{\eta max}$

R_1^{SR} = Spin-rotation relaxation rate = $R_1 - R_1^{DD}$

τ_c = Correlation time.

R_1^{SR}. The only compound in Table V that does not fit into this generalisation is bis(tri-n-butyltin) oxide (8), which may be seen to have the lowest dipolar contribution. This is probably due to the fact that although the molecular weight is higher than for most of the carbohydrate derivatives, the chain structure of butyl groups permits the molecule to tumble in solution more freely than occurs from the 'paddle-like' nature of the carbohydrate. There is a parallel increase in the spin-rotation contribution.

It is accepted that intermolecular dipolar contributions to the relaxation are generally small, and so the large nuclear Overhauser effect (N.O.E.) encountered must be intramolecular, arising from protons on the alkyl chain. If a fixed zig-zag orientation of an n-alkyl group is assumed,



the distance from the Sn nucleus to the α-proton is found to be 275 pm, and to the β-proton 325 pm.[27] The dipolar relaxation rate, R_1^{DD}, is related to the proton-metal internuclear distance, r_{X-H}, by the expression

$$R_1^{DD} = \frac{\gamma_X^2 \gamma_H^2 \hbar}{r_{X-H}^6} \tau_c$$

where γ_X and γ_H are the magnetogyric ratios of the nucleus X and H respectively, and $\hbar$ is Planck's constant divided by 2π. The relative contributions of α- and β- protons to dipolar relaxation of tin may, therefore, be calculated from the r^6_{X-H} dependence, and are given below:

	r_{Sn-H} (pm)	relative effectiveness
α-proton	275	1.00
β-proton	325	0.37

The contribution from the β-proton although being only about 37% that of an α-proton is still a significant quantity. From the equation shown above it can be seen that the correlation time, τ_c, may be calculated from a knowledge of the dipolar relaxation rate. However, the number of contributing protons must also be included in this expression (a tri-n-butylstannyl groups has 6α- and 6β-protons) and so the r^{-6} term must be replaced by $\sum_{N_\alpha} r_\alpha^{-6} + \sum_{N_\beta} r_\beta^{-6}$ where r_α, r_β are the Sn-H internuclear distances and N_α, N_β the number of contributing protons. The calculation of correlation times assumes isotropic motion of the molecule in solution and a rigid alkyl chain. For the compounds studied obviously neither situation will apply. But within any series of closely related molecules the degree of error associated with each assumption will be similar. Consequently, correlation times were calculated and are included in Table V. By comparing the values obtained for the organotin - carbohydrate derivatives it can be seen that the smaller the molecule, the shorter the correlation time, τ_c. This is presumably because it can reorient more easily, due to fewer solvent molecules having to be swept out of the way for rotation to occur. The decreased efficiency of dipolar relaxation for the smaller molecules is paralleled by an increased efficient spin-rotation relaxation.

Compounds (4) and (6), the mono- and di-O-tributylstannyl ethers of methyl 4,6-O-benzylidene-α-D-glucopyranoside, provide an interesting situation because it is possible to see the effect made upon the tin attached to C-3 by further tributylstannylation at C-2. In (4), τ_c is 183 psecs. and this is slowed to 263 psecs. by substituting the C-2 position. If the spin-lattice relaxation time and nuclear Overhauser effect of compound (5) had been measured, it would have been possible to see the effect upon tin at C-2 by further substitution at C-3 and to tell if an increase in τ_c of the order of 60 psecs. is usual for such reactions. Unfortunately such measurements were not made upon (5) due to the relatively low concentration of the compound, Table I.

So far the results have been discussed purely in terms of the size and nature of the species concerned. However, a very important consequence of the large dipolar contribution to the spin-lattice relaxation is that it is necessary to record the ^{119}Sn F.T.N.M.R. spectra of these compounds using N.O.E. suppressed conditions (Section 1.5.1.6.). The dramatic effect of not suppressing the N.O.E. is illustrated in Figure IIIa and IIIb; in (b) there is a stronger N.O.E. on the two larger peaks giving a negative intensity, than on the three smaller features, their intensity being reduced to zero. The ^{119}Sn spectrum of the product of the reaction of bis(tri-n-butyltin) oxide with methyl 4,6-O-benzylidene-α-D-glucopyranoside was expected to show just two peaks, corresponding to a tributylstannyloxy group at both the C-2 and C-3 positions. As such, if normal ^{1}H decoupling had been used, the spectrum shown in Figure IIIb would have been assumed to be correct and the other peaks, Figure IIIa, would never have been observed. Thus, it is recommended that gated ^{1}H decoupling (Section 1.5.1.6.) be used, as a matter of precaution, when obtaining ^{119}Sn spectra of alkyltin compounds, where the alkyl chain contains three or more carbon atoms.

4.3. Summary

This work has demonstrated the benefits of a multi-nuclear N.M.R. investigation. The simple form of the ^{119}Sn spectrum readily indicates the number, coordination state and relative amounts of tin species present. As yet, the ^{119}Sn chemical shift is not indicative of the position of substitution onto the carbohydrate ring or of the anomeric form. But, the former may be determined from the ^{13}C spectrum, where the appearance of ^{119}Sn satellites were an essential aid to assignment, and the latter from the ^{1}H spectrum. Thus, it may be seen that an N.M.R. investigation of a compound by any single nucleus, although yielding much information does have some disadvantages, but that a multi-nuclear investigation is a very powerful tool for structural analysis.

4.4. Experimental

The di- and tri-n-butylstannyl ethers were prepared by azeotropic dehydration of dibutyltin oxide or bis(tributyltin) oxide with the appropriate sugar in boiling toluene. Compounds (1)-(3) and (7) have been prepared previously and their physical properties are described elsewhere.[6,7,10] Compounds (4)-(6) were not isolated and their N.M.R. spectra were recorded as mixtures. The organotin-carbohydrates are hydrolysed fairly rapidly by moisture and the solutions for N.M.R. measurements were prepared in a glove-box under an atmosphere of dry nitrogen. Toluene was de-gassed with dry nitrogen, prior to dissolution of the compound. The ease of hydrolysis of the organotin-carbohydrate derivatives may be compared to the inert behaviour towards similar reaction of the organotin derivatives of 3-hydroxyflavone (Section 3.6), where intramolecular coordination from a carbonyl group to the tin atom imparts stability.

N.M.R. spectra were recorded at 25^{0}C with JEOL FX90Q or JEOL FX100Q instruments, using 10 mm. tubes and an internal deuterium lock on approximately 10% internal hexadeuteriobenzene. All ^{119}Sn spectra were recorded with gated ^{1}H decoupling (Section 1.5.1.6), to suppress the nuclear Overhauser effect, N.O.E. Spin-lattice relaxation times were measured using the 180^0-τ-90^0 pulse technique (Section 1.5.1.5.) and the nuclear Overhauser factor, η, was determined by recording the ^{119}Sn spectrum with and without the N.O.E., (Section 1.5.1.6.).

4.5. References

1) A.J. Bloodworth and A.G. Davies in 'Organotin compounds,' Vol. 1, Chapter 4. Ed. A.K. Sawyer, Marcel Dekker Inc., New York, 1971.

2) I.D. Jenkins, J.P.H. Verheyden and J.G. Moffatt, J. Am. Chem. Soc., 1971, 93, 4323.

3) D. Wagner, J.P.H. Verheyden and J.G. Moffatt, J. Org. Chem., 1974, 39, 24.

4) P.J. Smith, Chem. Ind. (London) 1976, 1025.

5) T. Ogawa, Kagaku To Seibutsu, 1974, 14, 654.

6) A.J. Crowe and P.J. Smith, J. Organomet. Chem., 1976, 110, C57.

7) A.J. Crowe Ph.D. Thesis, London 1980.

8) M.J. Robins, A.S.K. Lee and F.A. Norris, Carbohydr. Res., 1975, 41, 304.

9) G.F.J. Chittenden, Carbohydr. Res., 1979, 74, 333.

10) S. David, C. Pascard and M. Cesario, Nouveau J. Chim., 1979, 3, 63.

11) L. Pellerito, G. Ruise, R. Barbieri and M.T. LoGuidice, Inorg. Chim. Acta, 1977, 21, L33.

12) P.J. Smith and A.P. Tupciauskas Annu. Rep. N.M.R. Spectrosc., 1978, 8, 291.

13) A.G. Beaumont and C.A. Mackay, Int. Pest. Control, 1974, 16, 8.

14) T. Ogawa and M. Matsui, Carbohydr. Res., 1977, 56, C1.

15) J.C. Pommier and J. Valade, J. Organomet. Chem., 1968, 12, 433.

16) J. Mendelsohn, J.C. Pommier and J. Valade, Compt. Rend., Ser. C, 1966, 263 921.

17) J.C. Pommier, F. Mendes and J. Valade, J. Organomet.Chem., 1973, 55, C19.

18) E. Conway, R.D. Guthrie, S.D. Gero, G. Lukacs, A.M. Sepulchre, E.W. Hagaman and E. Wenkert, Tetrahedron Lett., 1972, 4879.

19) A.G. Davies, D.C. Kleinschmidt, P.R. Palan and S.C. Vasishtha, J. Chem. Soc., C, 1971, 3972.

20) V.S. Petrosyan, Progr. N.M.R. Spectrosc., 1977, 11, 115.

21) J.E. Sarneski, L.E. Erickson and C.N. Reilly, J. Magn. Reson., 1980, 37, 155.

22) Y.C. Puskar, T.A. Saluvere, E.T. Lippmaa, A.B. Pernin and V.S. Petrosyan, Doklady Akad. Nauk. SSSR, 1975, 220, 112.

23) C.R.E. Lassigne, Ph.D. Thesis, Simon Fraser Univ., 1975.

24) C.R.E. Lassigne and E.J. Wells, J. Magn. Reson., 1977, 26, 55.

25) R.R. Sharp, J. Chem. Phys., 1972, 57, 5321.

26) M.J. Ahmed, Ph.D. Thesis, Univ. of London, 1977.

27) A. Frangou, Ph.D. Thesis, Univ. of London, 1979.

Fluorimetric Determination of Triphenyltin Compounds in Water

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Keywords: *Triphenyltin compound determination*; *3-hydroxyflavone*; *spectrofluorimetry*; *water analysis*

Triphenyltin compounds, both as the acetate and hydroxide, are extensively used as fungicides for the control of the potato blight fungus *Phytophthora infestans* and also in certain anti-fouling paints. The toxicity of these compounds has been assessed[1] and a large degree of species variation has been observed, and with the increasing concern about environmental pollution, methods for the determination of fungicides and pesticides at very low concentrations are becoming increasingly important.

It has been shown that under laboratory conditions triphenyltin compounds degrade to inorganic tin[2,3] by the action of both light and micro-organisms present in the soil, although Barnes *et al.*[3] could find no evidence of leaching from soil under laboratory conditions. Because of the manner in which the compounds are applied (aerial spraying) there is the possibility that ponds, streams and rivers could be contaminated, either by air-borne spray or by run-off water from fields adjacent to waterways. In marine anti-fouling systems, where leaching of trace amounts of the compounds is inevitable, the determination of triphenyltin compounds at sub-parts per million levels is important as triphenyltin compounds are relatively toxic to aquatic life.[4]

Sub-microgram amounts of triphenyltin compounds have been determined both spectrofluorimetrically[5] and by anodic-stripping voltammetry.[6] Woggan and Jehle[7] used the latter method for the determination of tributyltin oxide and triphenyltin compounds in water (at the 0.01 p.p.m. level) after steam distillation and thin-layer chromatography (tributyltin) or solvent extraction and thin-layer chromatography (triphenyltin). However, as anodic-stripping voltammetry requires elaborate instrumentation, it was decided to investigate the possibility of using spectrofluorimetry for the determination of triphenyltin compounds in water. Coyle and White[8] showed that 3-hydroxyflavone could be used to determine sub-microgram amounts of tin and Vernon[5] used the reagent to determine triphenyltin residues in potatoes. The work described here is based on this procedure, although it was not found possible to reproduce some of the earlier findings.[5]

Experimental

Apparatus and Reagents

All fluorescence measurements were made with a Perkin-Elmer, Model 1000, fluorescence spectrophotometer, with suitable filters for the isolation of excitation wavelengths.

Procedure

Shake 50 ml of the water sample with 10 ml of toluene in a separating funnel for approximately 30 min and allow the two layers to separate.

For the determination of triphenyltin compounds in the range 0.2–2.0 p.p.m. add 1.0 ml of the toluene layer to 5.0 ml of a 0.01% solution of 3-hydroxyflavone in toluene and 1 ml of a saturated aqueous solution of sodium acetate in a stoppered container (*e.g.*, a 10-ml calibrated flask) covered with black paper and shake for approximately 10 min. Measure the fluorescence emission of the organic layer at approximately 495 nm, using an excitation wavelength of approximately 415 nm. For the 0.004–0.2 p.p.m. range of triphenyltin compounds add 5.0 ml of toluene layer to 1.0 ml of 3-hydroxyflavone solution and 1 ml of saturated sodium acetate solution and continue as above. Prepare a reagent blank by shaking 50 ml of water free from triphenyltin with 10 ml of toluene and continue as above.

Calibration

Prepare calibration graphs by mixing known volumes of triphenyltin chloride solutions (5×10^{-7}–5×10^{-6} M) in toluene with either 1.0 or 5.0 ml (as appropriate) of 0.01% solution of 3-hydroxyflavone in toluene and make the final volume up to 6 ml. Shake with 1 ml of saturated aqueous sodium acetate solution in a darkened container for approximately 10 min and measure the fluorescence as before.

Results

Samples of distilled water, tap water, canal water and synthetic sea water (prepared according to BS 3900: Part F4[10]) were spiked with standard solutions of triphenyltin chloride in ethanol, and Table II shows the results for the extraction and determination procedure.

TABLE II

RECOVERIES OF TRIPHENYLTIN CHLORIDE IN WATER

Concentration of triphenyltin, p.p.m.	Solvent grade	No. of extractions (all types of water)	Average recovery, %	Standard deviation, σ_{n-1}, %
2.0	AnalaR	7	93.6	4.2
0.2	AnalaR	18	89.4	4.9
0.02	AnalaR	4	88	10.9
0.008	AnalaR	10	82.9	11.9
0.004	AnalaR	17	74.0	11.3
0.004	Aristar	16	78.6	8.9

Table III shows the effect on the blank readings of using the two grades of toluene. The average blank readings given were obtained with the spectrofluorimeter set to read 0 and 300 on the emission scale for calibration over the range 0–0.1 μg of triphenyltin chloride per 6 ml.

TABLE III

EFFECT OF THE SOLVENT GRADE ON THE REAGENT BLANK

Solvent grade	No. of readings (all types of water)	Average blank	Standard deviation, σ_{n-1}
AnalaR	11	13.8	17.8
Aristar	20	4.4	7.7

Discussion

Barnes *et al.*[3] showed that triphenyltin acetate hydrolyses rapidly to the hydroxide in the presence of large amounts of water and therefore any solubility figures for the triphenyltin acetate in water are in fact for the hydrolysed product. They found this value to be approximately 3 p.p.m. in distilled water.

The present work has shown that triphenyltin compounds in water at concentrations of 0.004–2 p.p.m. are readily extracted into toluene and can be determined by spectrofluori-

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MULTI-NUCLEAR (^{119}Sn, ^{13}C, ^{1}H), FOURIER-TRANSFORM, N.M.R. STUDIES OF DI- AND TRI-BUTYLSTANNYL ETHERS OF CARBOHYDRATES

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ABSTRACT

^{119}Sn-N.m.r. spectra are reported for toluene solutions of the tributylstannyl ethers of 2,3,4,6-tetra-*O*-methyl-D-glucose, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, methyl 2,3-di-*O*-methyl-α-D-glucopyranoside, and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, and the dibutylstannyl ether of the last sugar. In the reaction of bis(tributyltin) oxide with methyl 4,6-*O*-benzylidene-α-D-glucopyranoside in toluene, HO-3 is much more reactive than HO-2. The presence of the various tin-containing species is readily apparent from the ^{119}Sn-spectra. The importance of suppressing the nuclear Overhauser effect is demonstrated. The appearance of ^{119}Sn satellites in the ^{13}C-n.m.r. spectra demonstrates couplings of the types, $^{2}J(^{119}\text{Sn-O-}^{13}\text{C})$ and $^{3}J(^{119}\text{Sn-O-C-}^{13}\text{C})$, for the first time, and, together with the ^{13}C-chemical shifts, facilitates the determination of the site of substitution. The ^{119}Sn-chemical shifts show that different states of coordination may be recognised. However, although different sites of substitution produce separate resonances, no simple relationship between shift and position is found. ^{13}C-Chemical shifts are reported for methyl 4,6-*O*-benzylidene-α-D-glucopyranoside and its tributylstannyl ethers, and substituent effects are discussed.

INTRODUCTION

Since the pioneering work of Moffatt and his colleagues[1,2], di- and tri-butylstannyl ethers have found wide use in carbohydrate chemistry[3,4]. More recently, certain inorganic tin salts, *e.g.*, $SnCl_2$, have been utilised as catalysts for the mono-

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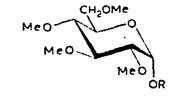
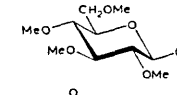
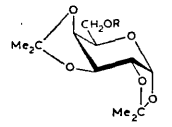
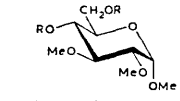
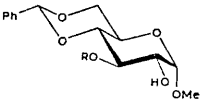
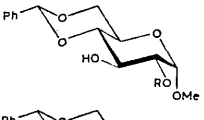
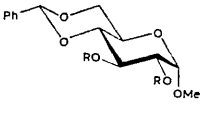
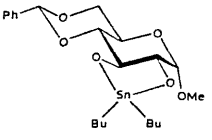
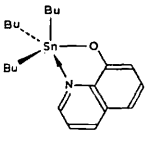
0008-6215/81/0000–0000/$ 02.50,

TABLE I

^{119}Sn-CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] FOR SOME ORGANOTIN-CARBOHYDRATE DERIVATIVES IN TOLUENE SOLUTION

Compound (R = Bu_3Sn)		*Approximate concentration* (M)	$\delta(^{119}Sn)$	$^2J(^{119}Sn\text{-}O\text{-}^{13}C)$	$^3J(^{119}Sn\text{-}O\text{-}C\text{-}^{13}C)$
	1a	0.2	99.0[c]	24	16
	1b	0.9	86.4[c]	23	13
	2	1.1	98.7	46	29[d]
	3	1.2	92.8[e] 98.6[e]	[f]	[f]
	4	0.2	101.8[g]	29	~18 (C-4) ~20 (C-2)
	5	0.05	87.3[g]	[h]	[h]
	6	0.4	77.5 (C-2)[g] 91.2 (C-3)[g]	29 (C-2) 28 (C-3)	19 (C-1) 22 (C-2) 16 (C-3) <18 (C-4)[i]
	7	0.6	−131.6[j]	12[e,k] <10[e,i,k]	34 (C-4)[k] 20 (C-1)[k]
$Bu_3SnOSnBu_3$	8	50% v/v	82.8[l]	[f]	[f]
	9	Neat liquid	29.0[m]	[f]	[f]
$Bu_2Sn(OMe)_2$	10	Neat liquid	−165.0[m]	[f]	[f]

[a]In p.p.m. downfield from Me_4Sn; error in $\delta(^{119}Sn)$ is ±0.2 p.p.m. for all compounds except **9** and **10**, for which it is ±4.0 and ±2.0 p.p.m., respectively. [b]In Hz; estimated error is ±1 Hz. [c]Recorded as a mixture of two anomers. [d]A possible alternative assignment, with this as a 4-bond coupling to C-4, was considered unlikely. [e]Assignment uncertain. [f]Not recorded. [g]In a mixture of **4**, **5**, and **6**. [h]No satellites were observable, due to low concentration. [i]Not resolved. [j]Ref. 7 reports −132.0 p.p.m. converted to Me_4Sn. [k]These couplings involved two different bonding-pathways. [l]Ref. 10 reports 77.8–84.5 p.p.m. [m]From ref. 10.

methylation of the *cis*-diol system in nucleosides[5] and carbohydrates[6] by diazomethane. There are, however, very few structural studies of these tin–carbohydrate derivatives[7-9] and it is not known for certain how tin is involved in the catalysis of the monomethylation of sugars by stannous salts, although a tin(II)–sugar intermediate has been proposed[3].

Fourier-transform (F.t.) n.m.r. spectroscopy, although used extensively to study ^{13}C nuclei, has only very recently been applied[10] to ^{119}Sn. We now report studies of a series of di- and tri-butylstannyl ethers of simple carbohydrates by this technique.

DISCUSSION

^{119}Sn-Chemical shifts

The ^{119}Sn-chemical shifts, δ (^{119}Sn), for the compounds studied are recorded in Table I, and a typical ^{119}Sn-spectrum, obtained for the product of the reaction between bis(tributyltin) oxide and 2,3,4,6-tetra-*O*-methyl-D-glucose in toluene, is shown in Fig. 1.

The spectrum reveals two ^{119}Sn-resonances, separated by 12.6 p.p.m., of which the more intense may be identified by inspection of the anomeric doublets in the ^1H spectrum, where the more intense doublet (δ 4.77, J ~6 Hz) is assigned to the β anomer (**1b**), and the less intense (δ 5.35, J ~4 Hz) to the α anomer (**1a**). The proportions of the anomeric species deduced from the ^{119}Sn peak-heights are 21% for **1a** and 79% for **1b**, values which are consistent with both the ^1H and ^{13}C spectra. These species are not in chemical equilibrium, as there was no temperature dependence

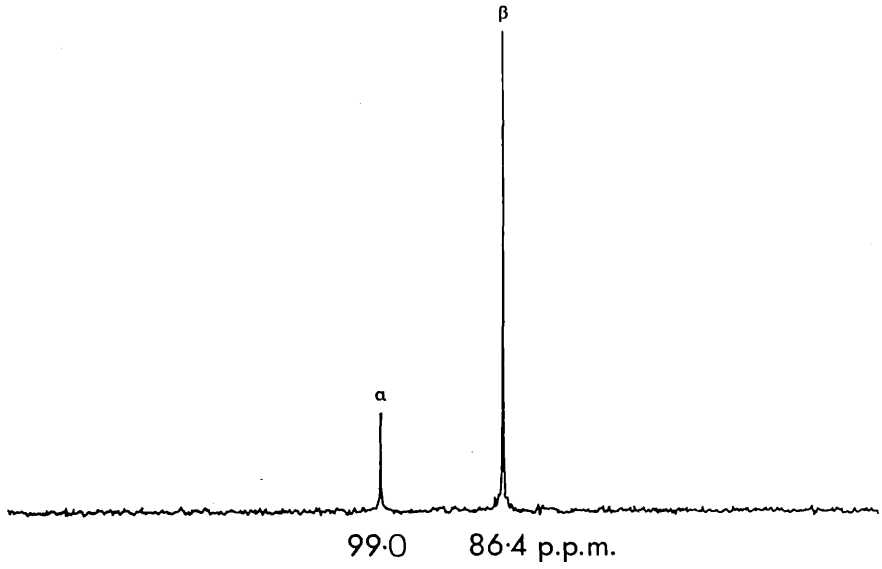


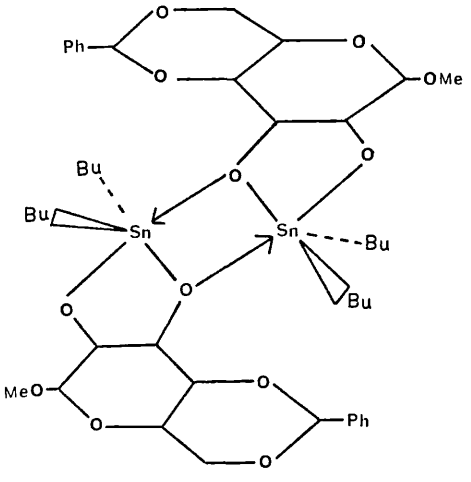
Fig. 1. ^{119}Sn-F.t.n.m.r. spectrum of the product of the reaction between bis(tributyltin) oxide and 2,3,4,6-tetra-*O*-methyl-D-glucose in toluene, at 37.08 MHz, recorded using 40 pulses.

of their relative concentrations. The preponderance of the β anomer contrasts with the equilibrium values (54% for α and 46% for β) determined from the ^1H spectrum (toluene) of the parent sugar, 2,3,4,6-tetra-*O*-methyl-D-glucose.

From the limited data available (Table I), it seems that changing the site of substitution by the tributylstannyl moiety, as in **3** and **6**, produces ^{119}Sn-shift differences which are comparable in magnitude to that observed between **1a** and **1b**. The ^{119}Sn-chemical shift for **2** is very similar to one of the values obtained for **3** (Table I). Since both compounds contain a tin substituent at C-6, this observation might indicate a relationship between the shift value and position of substitution. However, insufficient data are available to verify this possibility.

The tributyltin–carbohydrate derivatives and bis(tributyltin) oxide (**8**), showed ^{119}Sn resonances which were 70–100 p.p.m. downfield from that of tetramethyltin. This finding indicates[10] that the geometry at the tin atom in solution is tetrahedral and precludes the possibility of intramolecular coordination to tin. This argues against a previous suggestion[11] that, in a situation analogous to **6**, there was coordination between an equatorial tributylstannyl group at C-2 and the oxygen of an axial MeO-1 group.

It is well established that coordination at tin leads to significant shifts to higher fields. For example, in tributyltin 8-hydroxyquinolate (**9**), which contains[12] an intramolecularly chelated, five-coordinate tin atom, there is a shift of ~50 p.p.m. to higher field (Table I). The dibutylstannylene derivative (**7**) of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, which, in the solid state and in solution, exists as a dimer (**11**) containing five-coordinate tin, shows a ^{119}Sn resonance at −131.6 p.p.m. This shift is similar in magnitude to that (−165 p.p.m., Table I) reported for $Bu_2Sn(OMe)_2$ (**10**), which has a similar, dimeric, oxygen-bridged structure. There was no evidence[7] for the alternative structure of the dimer **11**, which involves the donation of electrons from O-2 to tin.



11

Order of reactivity of the hydroxyl groups in methyl 4,6-O-benzylidene-α-D-glucopyranoside with bis(tributyltin) oxide (**8**)

The reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside with bis(tributyltin) oxide (**8**) in toluene, which had not been studied previously, follows a rather complicated pattern. After 4 h at reflux temperature, a ^{119}Sn spectrum (Fig. 2*a*) was obtained which showed five resonances. A 24-h treatment of the required stoichiometric quantities gave the 2,3-bis(tributylstannyl) ether (**6**), which showed the same two major resonances at 77.5 and 91.2 p.p.m. as before. The two peaks at 83.8 and 101.8 p.p.m. were also present, but at one-third of their previous, relative intensity. The small signal at 87.4 p.p.m. was no longer observed.

Addition of excess of sugar to the solution that gave the spectrum shown in Fig. 2*a*, followed by boiling under reflux for a further 12 h, resulted in the spectrum shown in Fig. 2*c*. Comparison with Fig. 2*a* shows that the peak at 83.8 p.p.m. has disappeared, whereas the resonances at 87.4 and 101.8 p.p.m. both increased in intensity. It thus appears that the resonance at 83.8 p.p.m. is due to unreacted **8**

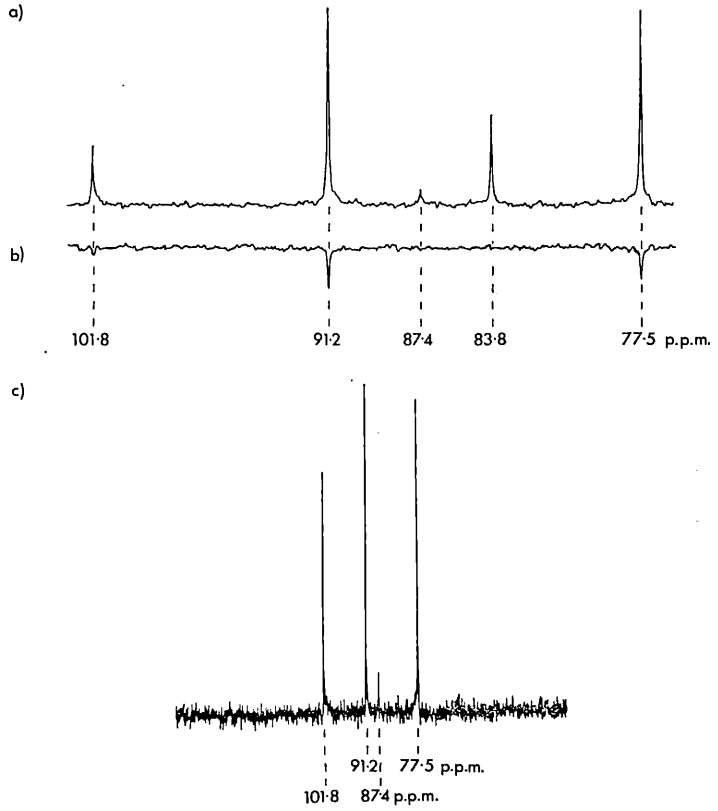


Fig. 2. ^{119}Sn-F.t.n.m.r. spectra of the products of the reaction of bis(tributyltin) oxide with methyl 4,6-*O*-benzylidene-α-D-glucopyranoside in toluene: (*a*) stoichiometric amounts boiled under reflux for 4 h; (*b*) as for (*a*), but with n.O.e; (*c*) solution (*a*) boiled for a further 12 h with excess of carbohydrate.

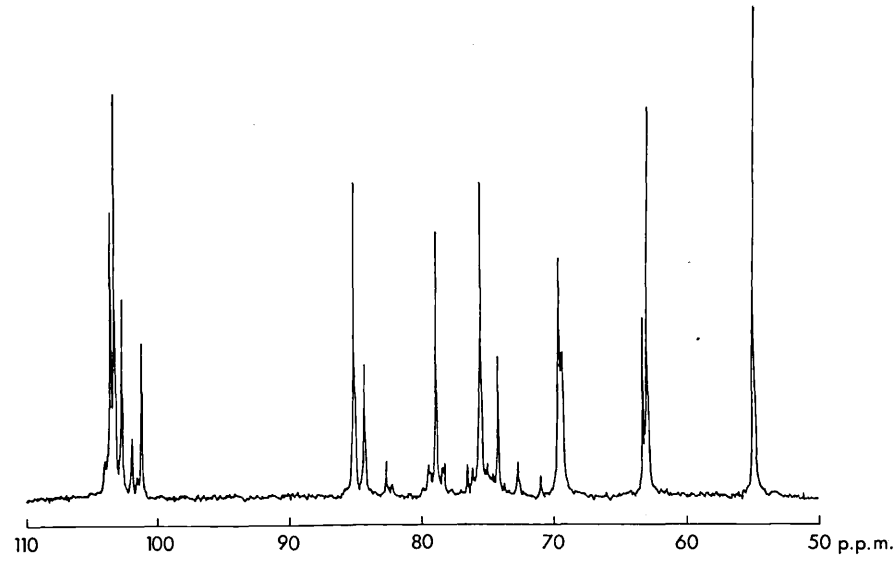


Fig. 3. ^{13}C-F.t.n.m.r. spectrum, showing the ring-carbon region, of the products of the reaction of bis(tributyltin) oxide with methyl 4,6-*O*-benzylidene-α-D-glucopyranoside in toluene (reflux, 4 h) recorded at 25.0 MHz, using 1000 pulses.

TABLE II

^{13}C-CHEMICAL SHIFTS[a] FOR SOLUTIONS OF METHYL 4,6-*O*-BENZYLIDENE-α-D-GLUCOPYRANOSIDE AND ITS TRIBUTYLSTANNYL DERIVATIVES **4–6** IN TOLUENE

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*OMe*
Parent sugar	100.4	73.5	72.1	81.5	62.9	69.1	101.9	55.0
4	101.0	74.1	75.4	84.1	63.2	69.2	102.6	54.9
5	[b]	76.3	72.5	82.4	[b]	[b]	[b]	54.9[c]
6	103.0	78.8	75.4	84.9	62.9	69.4	103.4	54.9

[a]In p.p.m. (±0.1) downfield from Me_4Si, measured from the methyl resonance of toluene, taken as 21.3 p.p.m.; chemical shifts of **4**, **5**, and **6** were recorded for a mixture. [b]Not assignable. [c]Presumed coincident with the methoxyl resonances of **4** and **6**.

(see Table I), while the resonances which increased in intensity correspond to the mono-*O*-tributylstannylated sugars. The peak at 101.8 p.p.m. was attributed to the preponderant monosubstituted derivative, the 3-tributylstannyl ether (**4**), by examination of the ^{13}C-n.m.r. spectra of the same solutions (see Fig. 3 and Table II). Similarly, the peak at 87.4 p.p.m. was assigned to the 2-substituted compound **5**, while those at 77.5 and 91.2 p.p.m. were assigned to the groups at positions 2 and 3, respectively, of the disubstituted derivative **6**.

The foregoing spectra indicate that O-3 is much more reactive to initial substitution than O-2. This inference was confirmed by a ^{13}C spectrum run after reaction

for 30 min, which showed that **4** and **6** were present in comparable amounts, but that the 2-tributylstannyl ether (**5**) was very much less evident. It seems that the conversion **4**→**6** occurs almost as easily as the initial substitution to form **4**, in contrast to the slow, initial substitution at position 2. This difference in reactivity of HO-2 and HO-3 to tributylstannylation has been noted[11] for other sugars.

Effect of substituents on ^{13}C resonances

The ^{13}C spectrum of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside in deuteriochloroform has been assigned previously[13] and matches the spectrum for a solution in toluene. The largest effects of tributylstannylation on the ^{13}C shifts (see Table III) are at the site of substitution: 3.3 p.p.m. for the C-3 derivative (**4**), 2.8 p.p.m. for the C-2 derivative (**5**), and 5.3 and 3.3 p.p.m. for the diether **6** at C-2 and C-3, respectively. Significant effects are observed at the carbon atom adjacent to the site of substitution, but not necessarily at both adjacent carbon atoms. For instance, the shift of 2.6 p.p.m. for the C-4 signal in **4** contrasts with that of 0.6 p.p.m. for C-2. With **5**, there is an insignificant effect (0.4 p.p.m.) for C-3, but, unfortunately, the C-1 signal was not assignable. For **6**, shifts of 2.6 and 3.4 p.p.m. were found for C-1 and C-4, respectively. The data for **6** may be rationalised in two ways. Starting with **4** and substituting at C-2, there are shifts of 2.0, 0, and 4.7 p.p.m. for C-1, C-3, and C-2, respectively. This pattern follows that for non-substituted, adjacent carbon positions and indicates a larger effect at C-2 when C-3 is tributylstannylated. An alternative approach is to start with **5** and substitute at C-3, where the shifts of 2.9 p.p.m. at C-3 and 2.5 p.p.m. at C-4 follow the original pattern. In this case, the same 2.5-p.p.m. shift is found at C-2, presumably because C-2 was already tributylstannylated.

For **7**, uncertainty in the assignment of the ^{13}C signals for C-2 and C-3 leads to two possible values for the substituent effects. However, the shift changes, with respect to the parent sugar, on dibutylstannylation are as follows: C-1, 5.0; C-2, 0.8 (6.1); C-3, 7.6 (2.3); C-4, 4.0; C-5, 2.8; C-6, 1.9; C-7, 3.9; and OMe, 1.4 p.p.m.; where the figures in parentheses denote the alternative assignment. Substituent effects for **7** are generally larger than those for **4**–**6**.

Since the dimeric structure **11** involves electron donation from O-3→Sn, it would

TABLE III

^{13}C-SUBSTITUENT EFFECTS[a] ON TRIBUTYLSTANNYLATION OF METHYL 4,6-*O*-BENZYLIDENE-α-D-GLUCOPYRANOSIDE

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*OMe*
4	0.6	0.6	3.3	2.6	0.4	0.1	0.7	−0.1
5	[b]	2.8	0.4	0.9	[b]	[b]	[b]	−0.1
6	2.6	5.3	3.3	3.4	0.0	0.3	1.5	−0.1

[a]Substituent effect in p.p.m. = δ (tributylstannyl derivative) − δ (parent sugar). [b]Peak not assigned.

be expected that this might lead to a deshielding of C-3, resulting in a significant shift to low field. Thus, the 7.6-p.p.m. substituent effect is the preferred assignment for this carbon resonance. The unusually small shift (0.6 p.p.m.) observed for C-2 presumably results from an unexplained shielding factor in the dimer.

Tin–carbon coupling constants

An interesting feature of the ^{13}C spectra of these derivatives is the appearance of ^{119}Sn satellites, an example of which is shown in Fig. 4. The satellites on C-1, arising from $^{2}J(^{119}Sn\text{-}O\text{-}^{13}C)$, and on C-2, arising from $^{3}J(^{119}Sn\text{-}O\text{-}C\text{-}^{13}C)$, are clearly visible for both anomers, and the magnitude of ^{3}J is less than that of ^{2}J. These couplings thus provide a valuable aid to assignment of the ^{13}C spectra. Although, to our knowledge, no $J(^{119}Sn\text{-}O\text{-}^{13}C)$ couplings have been observed previously, Davies *et al.*[14] observed $^{3}J(^{119}Sn\text{-}O\text{-}C\text{-}^{1}H)$ couplings in tributyltin alkoxides (Bu_3SnOR) only where R is very bulky. This effect was ascribed to a low rate of exchange of the alkoxy moieties in solution between different tin sites, and a similar situation would be expected to occur in the present case, when R is a large carbohydrate residue.

The cyclic substitution in **7** presents problems in the assignment of the couplings,

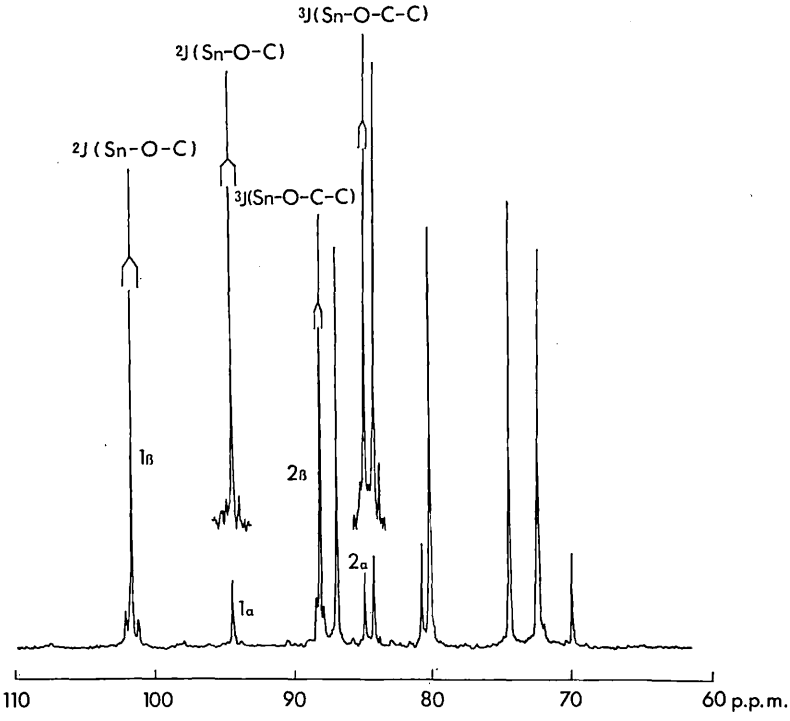


Fig. 4. ^{13}C-F.t.n.m.r. spectrum, showing the ring-carbon region, of the product of the reaction of bis(tributyltin) oxide with 2,3,4,6-tetra-*O*-methyl-D-glucose in toluene, recorded at 25.0 MHz, using 1000 pulses.

because the substituted carbon atoms each have two- and three-bond pathways to the tin atom. The contributions to the observed coupling will add algebraically[15]. The signals for **7** showing 34- and 20-Hz couplings (Table I) are assigned to C-4 and C-1, respectively, on shift arguments, but, unfortunately, similar arguments do not associate the 12-Hz coupling with C-2 or C-3 in particular. The couplings to C-2 and C-3 (12 and <10 Hz) are low compared to normal two-bond values and, presumably, result from algebraic addition of two- and three-bond contributions that are opposite in sign. In addition, in the ^{13}C spectrum of **7**, the butyl region showed two distinct sets of one-bond Sn-C couplings, indicating the non-equivalence of the butyl groups in the dimer **11**. The couplings were the same for both butyl groups, 614 and 588 Hz for ^{119}Sn and ^{117} Sn, respectively.

SUMMARY

The benefits of the multi-nuclear approach have been demonstrated. The simple form of the ^{119}Sn spectra readily indicates the number, coordination state, and relative amounts of tin species present, although the shifts in the carbohydrate derivatives are not as yet indicative of the position of substitution. The method allowed a qualitative indication of the relative reactivity of OH groups to tributylstannylation. The site of substitution was established *via* the ^{13}C spectra, where the appearance of ^{119}Sn satellites was an essential aid to assignment.

EXPERIMENTAL

The di- and tri-butylstannyl ethers were prepared by azeotropic dehydration of dibutyltin oxide or bis(tributyltin) oxide (**8**) with the appropriate sugar in boiling toluene. Compounds **1–3** and **7** have been described elsewhere[7,8]. Compounds **4–6** were not isolated and the n.m.r. spectra of mixtures were recorded. The organotin-carbohydrates are hydrolysed fairly rapidly by adventitious moisture, and the solutions for n.m.r. measurements were therefore prepared in a glove-box under an atmosphere of dry nitrogen. Toluene was de-gassed with dry nitrogen, prior to dissolution of the organotin-carbohydrate compound.

N.m.r. spectra were recorded at 25° with JEOL FX90Q or JEOL FX100Q instruments, using 10-mm tubes and an internal deuterium lock on $\sim 10\%$ internal hexadeuteriobenzene. It is essential that the ^{119}Sn spectra be recorded under conditions where the nuclear Overhauser effect (n.O.e.) is suppressed. Previous studies[16] have established the importance of intramolecular dipole–dipole relaxation of tin by the alkyl protons in tribultytin chloride, leading to a significant decrease in signal intensity under conditions of proton decoupling. This arises because ^{119}Sn has a negative magnetogyric ratio (*cf.* ^{15}N, ^{29}Si). The dramatic effect of not suppressing the n.O.e. is shown in Fig. 2; there is a stronger n.O.e. on the two larger peaks, giving a negative intensity, than on the three smaller features, their intensity being decreased to zero. Further details of spin–lattice relaxation times (T_1) and n.O. effects of these compounds will be reported elsewhere.

ACKNOWLEDGMENTS

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REFERENCES

1 I. D. JENKINS, J. P. H. VERHEYDEN, AND J. G. MOFFATT, *J. Am. Chem. Soc.*, 93 (1971) 4323–4324.
2 D. WAGNER, J. P. H. VERHEYDEN, AND J. G. MOFFATT, *J. Org. Chem.*, 39 (1974) 24–30.
3 P. J. SMITH, *Chem. Ind. (London)*, (1976) 1025–1029.
4 T. OGAWA, *Kagaku To Seibutsu*, 14 (1976) 654–657.
5 M. J. ROBINS, A. S. K. LEE, AND F. A. NORRIS, *Carbohydr. Res.*, 41 (1975) 304–307.
6 G. F. J. CHITTENDEN, *Carbohydr. Res.*, 74 (1979) 333–336.
7 S. DAVID, C. PASCARD, AND M. CESARIO, *Nouveau J. Chim.*, 3 (1979) 63–68.
8 A. J. CROWE AND P. J. SMITH, *J. Organomet. Chem.*, 110 (1976) c57–c59.
9 L. PELLERITO, G. RUISI, R. BARBIERI, AND M. T. LO GUIDICE, *Inorg. Chim. Acta*, 21 (1977) L33–L35.
10 P. J. SMITH AND A. P. TUPČIAUSKAS, *Annu. Rep. NMR Spectrosc.*, 8 (1978) 291–370.
11 T. OGAWA AND M. MATSUI, *Carbohydr. Res.*, 56 (1977) c1–c6.
12 A. G. BEAUMONT AND C. A. MACKAY, *Int. Pest Control*, 16 (1974) 8–12.
13 E. CONWAY, R. D. GUTHRIE, S. D. GERO, G. LUKACS, A. M. SEPULCHRE, E. W. HAGAMAN, AND E. WENKERT, *Tetrahedron Lett.*, (1972) 4879–4882.
14 A. G. DAVIES, D. C. KLEINSCHMIDT, P. R. PALAN, AND S. C. VASISHTHA, *J. Chem. Soc., C*, (1971) 3972–3976.
15 J. E. SARNESKI, L. E. ERICKSON, AND C. N. REILLY, *J. Magn. Reson.*, 37 (1980) 155–158.
16 A. FRANGOU, Ph.D Thesis, University of London, 1979.

THE PREPARATION OF SOME WATER SOLUBLE TRIBUTYLTIN BIOCIDES

by

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The preparation of some water soluble tributyltin biocides

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It is shown that introduction of an alkanesulphonyl radical into tributyltin biocides substantially increases their solubility in water without the necessity of adding an emulsifying agent, such as a quaternary ammonium salt.

Introduction

Tri-*n*-butyltin compounds, Bu_3SnX (X = inorganic radical), are widely used industrially as biocidal additives in marine antifouling paints[1], as fungicides in paint formulations[2], as wood preservatives[3] and in many other biocidal applications[2]. Although their biological activity against most types of fungi and gram positive bacteria is excellent[1–4], the compounds so far used for these applications do, however, suffer from the disadvantage of having a very low solubility in water (*e.g.* 0.001% w/v for bis(tributyltin) oxide at 25°C). This precludes their use for biocidal applications which require an aqueous carrier, where a concentration of 0.5 – 1.0% of the organotin compound would normally be required.

One way to overcome this problem has been to emulsify the tributyltin biocide, such as bis(tributyltin) oxide, with a suitable quaternary ammonium salt to produce a water-dispersible concentrate. Formulations of this type are used extensively for the eradication of moss, algae and lichens on stonework[5] and are currently under development as wood preservatives[6].

A second, more desirable approach to the problem is to synthesise a discrete, water soluble tributyltin fungicide. A number of novel anionic[7,8] tributyltin salts of general formula $(R_4P)^+(Bu_3SnCl_2)^-$ and their cationic[8] analogues, $(Bu_3SnL_2)^+BPh_4^-$, where L = DMSO, Ph_3PO, Ph_3AsO etc., were subsequently prepared in these laboratories but were found to be substantially insoluble in water. Similar tributylthiotin biocides, such as $Bu_3SnSCH_2CO_2^-Na^+$, where the tributyltin moiety is also part of an anionic residue have been reported[9] to be water soluble, but no quantitative data were given. In a recent publication, Suzuki and his co-workers claim[10] that tributyltin methane- and ethane-sulphonate are soluble in water to the extent of 3–10% and a systematic study of compounds of the type RSO_3SnBu_3 has therefore been carried out to determine the effect of the R group on the solubility.

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Results and discussion

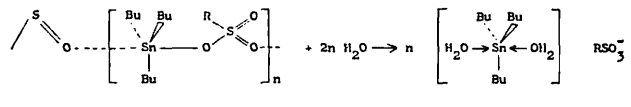
The water solubilities of the various tributyltin alkane- and arene-sulphonates studied are listed in Table 1.

Table 1: Water solubilities of RSO_3SnBu_3 compounds at 25°C

R in RSO_3SnBu_3	w/v % Solubility of Compound (± 0.1) After 1 day	1 month	2 months
Ph	0.2	0.5	0.6
C_6H_4Me–4	0.4	0.4	[a]
C_6H_3Cl–4,NH_2–5	0.06	[a]	[a]
CF_3	0.1	0.7	0.8
Me	1.1[b]	⩾1.6[c]	⩾1.6[c]
Et	1.5[b]	1.9	1.9[d]
^{n}Bu	0.8	0.8	0.8
^{t}Bu	0.7	0.8	0.8
NH_2	0.6[e]	1.3	1.6
$N(SnBu_3)_2$	0.05	0.3	0.6

[a]Not performed. [b]Ref. 10 reports 3-10%. [c]The initial solution was a nominal 1.5% w/v. [d]1.8% after 6 month. [e]Ref. 11 reports 22%.

The results show that, in general, the water solubility of the RSO_3SnBu_3 compounds increases with the electron-releasing power of the R group and that a maximum is attained when R = Et. A further increase in chain length of the *n*-alkyl group causes a drop in solubility. The solubilities of most of the compounds were found to rise to a maximum value on standing for a period of time (see Table 1) and this may be attributed to the ease with which the water molecules are able to break up[12] the self-associated polymeric structure (A), which is likely to exist in most of the pure compounds[13] (equation 1):



(A) (B) .....(1)

The aqueous solubilities found for the tributyltin alkane-sulphonates (0.7–1.5% w/v) are remarably high for tributyltin compounds and are in the range required for most biocidal applications. The pH values have been recorded for aqueous solutions of the Bu_3SnSO_3R compounds, where R = Me, Et, CF_3 and Ph, and indicate that these are fairly acidic (pH range: 2.5–2.8). Similar values have been observed previously[14] for aqueous solutions of other trialkyltin salts (*e.g.* Me_3SnBr) and were ascribed to the partial dissociation of the hydrated trialkyltin cation (equation 2):

$$\left[R_3Sn(H_2O)_2\right]^+ X^- \longrightarrow R_3SnOH + HX + H_2O \quad \text{.....(2)}$$

It is also clear from the results in Table 1 that the compound $(Bu_3Sn)_2NSO_3SnBu_3$ undergoes a slow hydrolysis of the Sn-N bonds to produce tributyltin sulphamate, which has a higher aqueous solubility (equation 3):

$$(Bu_3Sn)_2NSO_3SnBu_3 + H_2O \longrightarrow Bu_3SnOSnBu_3 + Bu_3SnSO_3NH_2 \quad \text{.....(3)}$$

An aqueous solution of tributyltin ethanesulphonate shows no appreciable decomposition on standing in normal daylight for at least 2–3 months, in agreement with earlier work[10]. The biocidal effectiveness of the tributyltin compounds does not appear to be reduced by their dissolution in water. For example, an aqueous solution of tributyltin methanesulphonate is claimed to have an activity comparable with that of the commercial biocide bis(tributyltin) oxide in fungicidal and bactericidal screen[10†]. The activity of aqueous solutions of these compounds as wood preservatives on a BS 838 wood block/agar test is currently under investigation at the I.T.R.I.

Preparation of RSO_3SnBu_3 compounds

The sulphonic acid starting materials were all obtained commercially except *tert*-butanesulphonic acid, which was a gift from Professor A. G. Davies, University College, London, and *n*-butanesulphonic acid, which was prepared by the oxidation of *n*-butanethiol with concentrated nitric acid[15]. Bis(tri-*n*-butyltin) oxide was a gift from Mr. D. Fysh, Albright and Wilson Ltd., Oldbury.

The tributyltin alkane- and arene-sulphonates were prepared by azeotropically dehydrating a mixture of the appropriate sulphonic acid (2 moles) and bis(tributyltin) oxide (1 mole) in boiling toluene for 2–4 hr., using a Dean and Stark trap (equation 4):

$$2\ RSO_3H + Bu_3SnOSnBu_3 \longrightarrow 2\ Bu_3SnSO_3R + H_2O \quad \text{.....(4)}$$

The products were obtained, after removal of the solvent, as clear viscous oils, which decomposed on attempted distillation *in vacuo*, or as pale yellowish-brown solids. The oils were found to occlude solvent molecules tenaciously and prolonged pumping at reduced pressure was therefore necessary for purification. Tributyltin *tert*-butanesulphonate readily absorbs a molecule of water in air to form the monohydrate, *c.f.* $PhSO_3SnMe_3$, H_2O[13]. The melting points and analytical data for all compounds are shown in Table 2.

†Recent work[16] has also shown a molluscicidal activity comparable with that of bis(tributyltin) oxide in bioassays against the adult snail, *B. glabrata*, which is an intermediate host of schistrosomiosis.

Table 2: Analytical data for tributyltin alkane- and arene-sulphonates.

R in RSO_3SnBu_3	Microanalysis: Found (Calcd.) % C	H	S	M.P. (°C)
Ph	48.83 (48.32)	7.44 (7.16)	6.26 (7.16)	oil[a]
C_6H_4Me–4	49.68 (49.46)	7.49 (7.37)	6.65 (6.94)	91–2
C_6H_3Cl–4,NH_2–5	43.45 (43.50)	6.53 (6.45)	6.30[b] (6.45)	158–9
CF_3	35.09 (35.54)	6.37 (6.15)	6.90 (7.29)	20–2
Me	39.87 (40.51)	7.81 (7.79)	8.72 (8.31)	oil[a,c]
Et	41.10 (42.10)	7.77 (8.02)	7.56 (8.02)	oil[a]
^{n}Bu	45.22 (44.96)	8.53 (8.43)	7.47 (7.49)	oil[a]
tBu[d]	43.17 (43.14)	8.18 (8.53)	6.83 (7.19)	61–4
NH_2	38.17 (37.31)	7.96 (7.51)	7.31[e] (8.29)	oil[a,f]
$N(SnBu_3)_2$	44.17 (44.81)	7.83 (8.40)	g —	oil[a]

[a]Decomposes on distillation. [b]Cl, 7.02 (7.15); N, 2.80 (2.82). [c]Ref. 10 reports $n_D^{24} = 1.490$. [d]Monohydrate. [e]N, 3.07 (3.63). [f]Ref. 11 reports $n_D^{25} = 1.4962$. [g]N, 1.71 (1.45); S not performed.

Reaction of sulphamic acid with bis(tributyltin) oxide

This reaction was found to follows two distinct paths depending on the temperature:

$$(Bu_3Sn)_2O + 2\ HO.SO_2.NH_2 \longrightarrow 2\ Bu_3SnO.SO_2.NH_2 + H_2O \quad \text{.....(5)}$$

$$(Bu_3Sn)_2O + 2\ HO.SO_2.NH_2 \longrightarrow 2/3\ Bu_3SnO.SO_2.N(SnBu_3)_2 + H_2O + 4/3\ HO.SO_2.NH_2 \quad \text{.....(6)}$$

If the azeotropic dehydration is carried out in refluxing benzene[11] or the two components are stirred together in toluene for 1 week at room temperature, tributylstannylation of the hydroxyl group is found to occur (equation 5). However, at higher temperatures, *e.g.* in refluxing toluene, tributylstannylation of both the hydroxyl and amino groups may be achieved (equation 6). In the latter case, the unreacted sulphamic acid may be filtered from the cooled reaction mixture, followed by removal of the solvent, to give tris(tributylstannyl) sulphamate as a pale yellow oil.

Preparation and analysis of aqueous solutions

Preliminary experiments were carried out to establish the nominal solubility of each compound to ensure that saturated solutions were attained. At least a 50% excess of each compound was used, except for tributyltin methanesulphonate, which was made up as a nominal 1.5% w/v aqueous solution. The saturated solutions were prepared by shaking the tributyltin compound with distilled water for 30 min. at 25°C and then left to stand overnight, to allow undissolved material to settle. Solutions were filtered if necessary and suitable aliquots subsequently taken after 1 day, 1 month and 2 months, the samples being stored in the dark.

The amount of the compounds retained in solution was determined by wet ashing the aliquot sample with nitric/sulphuric acids and determining the total tin content by iodimetric titration.

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References

1. Evans, C. J., Smith, P. J., *J. Oil Col. Chem. Assn.*, 58, 160 (1975)
2. Bokranz, A., Plum, H., *"Industrial Manufacture and Use of Organotin Compounds"*, Schering AG, Bergkamen, W. Germany, March 1975.
3. Richardson, B. A., *Rec. Brit. Wood Preserv. Assn. Ann. Conv.*, Cambridge, p.37 (1970)
4. Sijpesteijn, A. K., Luijten, J. G. A., van der Kerk, G. J. M., in *"Fungicides: An Advanced Treatise" (ed.* Torgeson, D. C.) Vol. 2, Academic Press, New York, p.331 (1969)
5. Richardson, B. A., *Stone Ind.*, 8, 2 (1973).
6. Richardson, B. A., Cox, T. R. G., *Tin and its Uses*, 102, 6 (1974)
7. Crowe, A. J., Smith, P. J., *Inorg. Chim. Acta*, 19, L7 (1976)
8. Crowe, A. J. Smith, P. J., Unpublished Work.
9. Wirth, H. O., Lorenz, H. J., Friedrich, H. -H., *U.S. Pat.*, 3,933,877 (1976)
10. Suzuki R., Kuriyama, Y., Shioyama, H., *Jap. Pat.*, 18,489 (1976)
11. Nakanishi, M., Tsuda, A. *Brit. Pat.*, 1,099,704 (1968).
12. Monaghan, C. P., Hoffman, J. F., O'Brien, E. J., Frenzel, L. M., Good, M. L., *Proc. 4th Control Rel. Pestic Symp.*, Oregon State Univ., USA, Aug. 1977.
13. Harrison, P. G., Phillips, R. C. Richards, J. A., *J. Organometal Chem.*, 114, 47 (1976)
14. Brinckman, F. E., Parris, G. E., Blair, W. R., Jewett, K. L., Iverson, W. P., Bellama, J. M., *Environ. Health Perspect.*, 19, 11 (1977) and references therein.
15. Vivian, D. L., Reid, E. E., *J. Amer. Chem. Soc.*, 59, 2559 (1935)
16. Smith, P. J., Crowe, A. J., Kumar Das, V. G. Duncan, J., *Pestic. Sci.* to be published.

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