MÖSSBAUER AND INFRARED STUDIES OF TRIPHENYLTIN CARBOXYLATES

by

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ABSTRACT

A study was undertaken to investigate the solid-state structure of about 25 triphenyltin carboxylates, $\emptyset_3SnOCOR$. The compounds were synthesized and then analyzed by Mössbauer and infrared spectroscopy.

The compounds were divided into three series on the basis of the nature of the R group. The first series of compounds had R groups which were "linear" chain hydrocarbons ranging in length from one carbon atom (triphenyltin formate) to eighteen carbon atoms (triphenyltin stearate). In the second series several compounds had methyl branches at various positions along the hydrocarbon chain, some had longer alkyl groups and a few had a methylene group bonded to the α-carbon atom. The third series contained mono-, di-, and tri-substituted haloacetates.

These compounds were prepared in order to test the assumption that bulky R groups would prevent (by steric interaction) polymer formation in the solid. The polymeric structure which is commonly found for triorganotin carboxylates consists of pentacoordinate Sn atoms. Each carboxylate group bridges between two different Sn atoms and this occurs indefinitely to form a polymer. Steric interaction of the R group with neighbouring phenyl groups (bonding to Sn) could prevent polymer formation. The resulting structure would be monomeric and have a tetracoordinate Sn atom and a terminal carboxylate group like that for an organic ester.

The majority of compounds were found to be polymeric solids. Structural changes (polymeric to monomeric) were observed for a few compounds

and this could be attributed to steric interaction. The Mössbauer and infrared data were complimentary and conclusive when used to differentiate between the two possible structural types.

In a polymeric structure the Sn atom can be visualized as being in a trigonal bipyramidal environment in which the oxygen atoms are axial and the phenyl groups equatorial. Using the above idealized structural type it was possible to test a point-charge model which had been used to predict quadrupole splitting values, Δ. The model was tested for the triphenyltin haloacetates and found to give fairly good agreement with the observed quadrupole splitting values.

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ACKNOWLEDGMENT

INTRODUCTION

In general, compounds having the formula $R_3SnOCOR'$ (R = alkyl or aryl and R' = alkyl) are polymeric in the solid state[1]. The tin atom is pentacoordinate with bridging carboxylate groups. In dilute solutions in non-polar solvents the compounds are monomeric with the tin atom being tetracoordinate.

Conclusions concerning the structures of these triorganotin compounds have been based mainly on infrared data and in particular on the position of the two C-O absorption bands for the solid and for a dilute solution of the compound in a non-polar solvent.[1],[2]. The solid state bands are similar to those of a salt-like or bridging carboxylate while the positions of the solution bands are much closer to those for an organic ester. It has also been observed that increasing the concentration of the solution increases the degree of polymerization. This is further support for a solid state structure that is polymeric rather than ionic.

Under certain conditions both of the C-O absorption band positions for the solid and solution are similar and are close to those of an organic ester. This occurs when the R group is bulky, for example when R = isoproxyl or cyclohexyl. Triisopropyltin acetate is a monomeric liquid[1] while tricyclohexyltin acetate[4] is a monomeric solid.

Janssen et al[1] have suggested that lengthening the R' group or introducing bulky R' groups may result in "destabilization of a polymeric structure by steric effect". Several compounds were studied in order to test this assumption.

A number of triphenyltin carboxylates, $\emptyset_3SnOCOR$, were prepared and their structural properties examined by Mossbauer and infrared spectroscopy. The first series of compounds (TABLES I, IV and VII) had R[*] groups which were linear chain hydrocarbons ranging in length from one carbon atom (triphenyltin formate) to eighteen carbon atoms (triphenyltin stearate). In the second series (TABLES II, V, and VIII) several compounds had methyl branches at various postions along the hydrocarbon chain, some had longer alkyl groups and a few had a methylene group bonded to the α-carbon atom.

There were several reasons for preparing a third series (TABLES III, VI, and IX) of compounds. The compounds were mono-, di- and tri- substituted haloacetates and the reasons are as follows. After observing the results for the compounds with more bulky groups on the α-carbon atom we concluded that it might be possible to determine a "critical size" (estimated in terms of a van der Walls radius) for α-carbon atom substituents. Substituents which were smaller than the "critical size" would give polymeric solids while those which were larger would give monomeric solids. There was some limitation (i.e. not conveniently available) in our choice of suitable halo-substituted acids with which to test thoroughly the previous hypothesis, however the infrared and Mössbauer results could be compared with those for the analogous tri-methyltin compounds.[5] As an added benefit, since a point-charge model[6-8] allows us to predict quadrupole splitting values for these compounds (assuming them to be isostructural with the corresponding tri-methyltin derivatives) our results can be used to test the predictive value of this model.

[*] Note the change from R' to R to refer to an organic group attached to the carboxylate part of the molecule.

FIGURE I shows the polymeric and monomeric structures for triorganotin carboxylates. When drawing the structures emphasis was placed on two important structural details. One is the environment of the Sn atom which is pentacoordinate in the polymer and tetracoordinate in the monomer. The two corresponding symmetry types are a trigonal bipyramid and a tetrahedron which represent an approximation to the actual structures. The other structural detail is the nature of the carboxylate group. In the polymer the carboxylate group is bridging while in the monomer the carboxylate group is terminal.

FIGURE I

Triorganotin carboxylates
$R_3SnOCOR'$
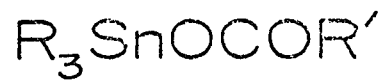
Polymeric structure
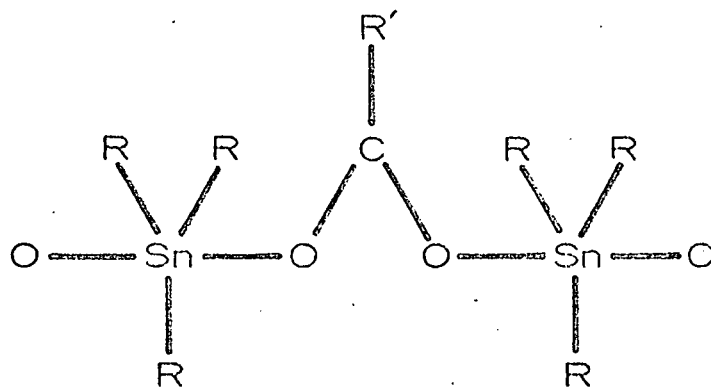
Monomeric structure
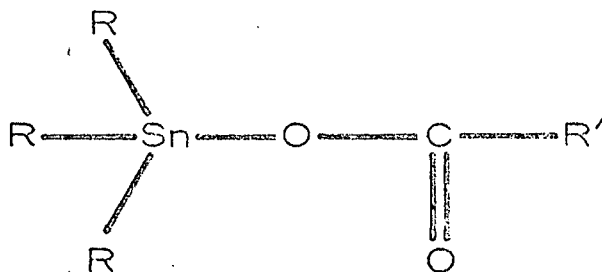
THE MÖSSBAUER EFFECT

Principles

The Mössbauer effect is the recoilless emission and resonant absorption of gamma radiation by nuclei bound in solids. The effect was discovered in 1957 and named after the discoverer Rudolph L. Mössbauer who received the Nobel Prize in Physics in 1961 for his work.

The following discussion will deal briefly with the principles of the Mössbauer effect and then with the applications to Chemistry. Firstly consider the case where a source and absorber are identical, that is the Mössbauer nuclei have the same chemical environment.

Normally it is difficult to observe resonance absorption of nuclear gamma radiation. This is because the free-atom recoil energy, E_R, lost by the photons during emission and absorption is larger ($\sim 10^5$) than the natural linewidths for emission and absorption. This means that, the energy of the emitted photon doesn't correspond to the energy required for absorption. If the emitting and absorbing atoms are confined to lattice sites and the recoil energy is less than the phonon energy or characteristic energy for lattice vibrations ($\sim 10^{-2}$ eV) then recoilless emission and resonant absorption can be observed when there is no thermal motion of the atoms in the lattice. Now the free-atom recoil energy approaches zero as the recoil mass gets very large by including many atoms in the lattice. Since the free-atom recoil energy is proportional to the square of the gamma-ray energy, the requirement of a "zero phonon"

event places a restriction on the energy of a Mössbauer transition. At present the practical limit is <150keV.

Mössbauer transition properties are given in TABLE A.

The Mössbauer effect is temperature dependent. A decrease in temperature increases the probability of a "zero phonon" event accompanying the emission and absorption of radiation. Due to the extremely low number of recoil-free processes at room temperature it was necessary to record Mössbauer spectra with the absorbers at a much lower temperature. It was convenient and relatively simple to maintain the absorbers at liquid nitrogen temperatures where a statistically significant Mössbauer effect could be determined after about ten to fifteen hours.

Chemical Applications

The applications of the Mössbauer effect to chemistry involve a situation where the absorber is not identical to the source and several different absorbers or chemical compounds are compared. In this experimental work there are two important Mössbauer parameters, the isomer shift and the quadrupole splitting, which give information about the chemical nature of compounds. Changes in the isomer shift and the quadrupole splitting are related respectively to changes in the electron density and distribution of electron density near the Sn nucleus. These changes are due mainly to valence electrons.

The chemical applications of the Mössbauer effect depend on

the extremely narrow linewidths which are characteristic of this type of radiation. The energy of the gamma ray is defined to within one part in 10^{12}, that is the width of a spectral line is 10^{-12} of the energy of the gamma ray. The interaction of electron and nuclear charge causes the transition energy for the source to be different from that for the absorber. These energy changes can be observed using a Mössbauer spectrometer since they are of the order of a linewidth or ~10^{-8} eV. Experimentally the energy difference is compensated for by Doppler shifting the source of gamma radiation by a few mm sec^{-1}. relative to a stationary absorber.

Isomer Shift

A Mössbauer transition occurs between the ground nuclear energy level and a low lying excited nuclear energy level. Emitting and absorbing nuclei which are in different chemical environments have different transition energies. This is a result of the interaction of electron charge with nuclear charge and is called isomer shift, I.S.

An equation for the isomer shift can be derived[9] by assuming that the nucleus is a uniformly charged sphere of radius R(dependent on the state of excitation) and that the electron charge density is uniform over nuclear dimensions. The isomer shift depends on the product of an electronic factor and a nuclear factor. The electronic factor is the electron charge density near the nucleus which is affected by the valence state of the Sn atom and the nuclear factor is the difference between the radius of the excited state and that of the ground state.

Experimental measurements[10] have shown that the nuclear

charge radius of the excited state is larger than that of the ground state

for ^{119}Sn which means that the sign of the difference is positive. This

holds true for all Sn containing compounds. Now it is possible to

relate an increase in isomer shift or a shift to higher energies with

an increase in electron density at the Sn nucleus for a particular absorber.

Since s-electron density has a finite probability of being at or near the

nucleus, changes in isomer shift are related to changes in s-electron

density. In Sn compounds, changes in isomer shift are due mainly to

changes in 5 s-electron density. These changes are a result of different

distributions of valence electron density.

A good example is grey Sn(α-Sn) which absorbs at -2.2 mm sec^{-1} [11]

higher in energy than stannic oxide, SnO_2. In SnO_2 there are Sn^{+4} ions

which are octahedrally surrounded by oxygen anions. The electronic con-

figuration of the Sn atom can be approximated by $[Kr]4d^{10}$. In grey Sn

each Sn atom is covalently bonded to four others which are at the corners

of a tetrahedron. The bonding can be considered as four sp^3 hybrid bonds

to each Sn atom and the electronic configuration can be approximated by

$[Kr]4d^{10}5S^15p^3$. The increase in isomer shift can be attributed to

the increase in 5S-electron charge density.

Experimentally the nuclear transition energy of the source is

compared with that for various absorbers. I.S. $= E_{ABSORBER} - E_{SOURCE}$.

It is conventional to report I.S. values relative to a reference absorber.

It is possible to report energy shifts relative to the source if the

NUCLEAR ENERGY LEVELS

ISOMER SHIFT, I.S.

$$I.S. = E_A - E_S$$

EXCITED STATE

GROUND STATE

E_O

E_S

SOURCE (S)

E_O

E_A
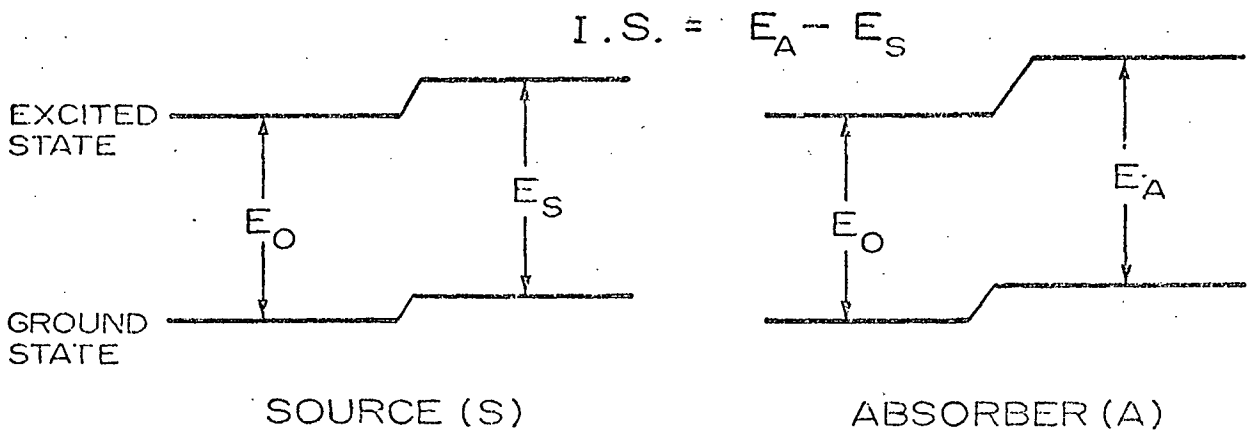
ABSORBER (A)

QUADRUPOLE SPLITTING, $\triangle$

$$\triangle = E_A\left(\tfrac{3}{2}\right) - E_A\left(\tfrac{1}{2}\right)$$

I

SUBSTATES

$\tfrac{3}{2}$

$\pm\tfrac{3}{2}$

$\triangle$

$\pm\tfrac{1}{2}$

E_A

$E\left(\tfrac{1}{2}\right)$ $E\left(\tfrac{3}{2}\right)$
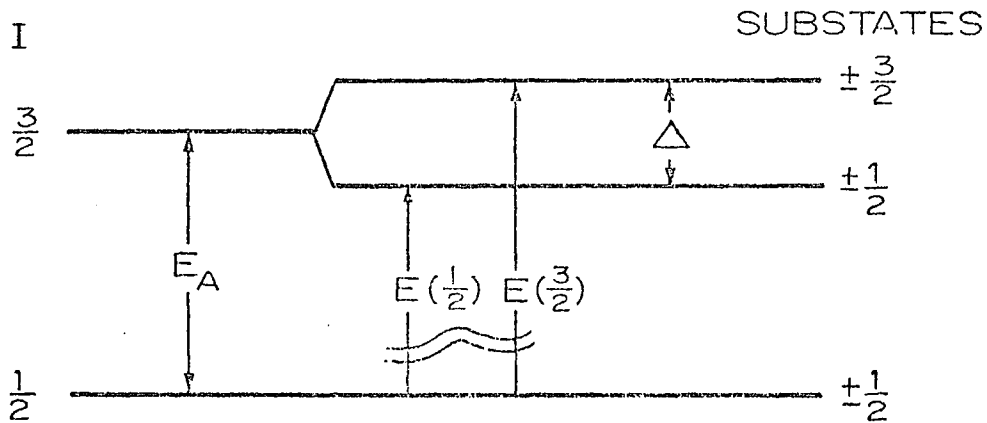
$\tfrac{1}{2}$

$\pm\tfrac{1}{2}$

FIGURE II

same compound is run as an absorber in order to determine a zero reference point on the energy scale.

For this experimental work the isomer shifts arereported relative to a popular reference absorber, SnO_2, which is arbitrarily set as 0 mm sec^{-1}, thus

$$\delta = (E_{ABSORBER} - E_{SnO_2}) \text{ mm sec}^{-1}$$

Quadrupole Splitting

Nuclear charge is not spherically symmetric when the nucleus has a spin quantum number greater than I = 1/2. Under these conditions the nucleus has a quadrupole moment and this occurs when the ^{119}Sn nucleus is excited (I = 3/2). If the electron charge is not uniformly distributed over nuclear dimensions then there will be an electric field gradient at the nucleus. The interaction of nuclear charge with the electric field gradient splits the energy of the excited state to give two excited substates and consequently two transitions in the Mössbauer spectrum. The energy difference between the two transitions is called the quadrupole splitting, Δ. The quadrupole splitting can be represented by:

$$\Delta = E_A(3/2) - E_A(1/2)$$

where the $\pm 3/2$ and $\pm 1/2$ are the quantum numbers for the two excited nuclear substates (FIGURE II).

The absence of splitting indicates a cubic or near cubic electron charge distribution such as tetrahedral or octahedral.

No contribution to the quadrupole splitting comes from non-bonding closed shells because they are spherically symmetric with respect to the nucleus. The same is true for S-electron density.

An asymmetric electron charge distribution comes mainly from charge density imbalances in valence electrons other than S-electrons. For example tetraphenyltin, $\emptyset_4$Sn, has no quadrupole splitting ($\Delta = 0$) but $\emptyset_3$SnCl has a quadrupole splitting of about 2.5 mm sec^{-1} [12]. In $\emptyset_4$Sn the coordination of the Sn atom is tetrahedral[13]. Since all four bonds to Sn are to phenyl C atoms the valence electron charge distribution will be uniform and hence $\Delta = 0$. In $\emptyset_3$SnCl a phenyl group has been replaced by a chlorine atom which has different bonding characteristics. This is sufficient to give a fairly large quadrupole splitting by causing an asymmetry in the valence charge distribution and also distorting the tetrahedral symmetry of the Sn atom.

EXPERIMENTAL

Mössbauer

(i) Source

The source of radioactivity was powdered barium stannate $BaSnO_3$, which had been enriched with the Mössbauer nucleide ^{119m}Sn and encapsulated in an acrylic plastic disc.* This was mounted on a larger disc which had been threaded at one end for easy attachment to the velocity transducer.

Barium stannate has extremely good Mössbauer properties. The emission line is unsplit and exhibits a narrow line width. It also shows one of the highest percentage effects ever reported in Sn Mössbauer spectroscopy. In particular this source had a line width of 1.13 mm sec^{-1} and a 25% effect. The average intensity of the source was about 4 millicuries (1 curie = 3.700 x 10^{10} disintegrations per second)[14]. Further Mössbauer transition properties of ^{119}Sn are given in TABLE A.

(ii) Absorber

The samples (triphenyltin carboxylates) were powdered and evenly packed into a circular brass cell with Mylar windows which were 1.25 cm. in diameter. With an absorber thickness of about 0.5 mm. it was possible to produce Mössbauer spectra with fairly narrow line widths ($\Gamma\sim 1.0$ mm sec^{-1}). The cell was inserted at the top of a copper tube which was immersed in

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* Commerical preparation by New England Nuclear Corporation, Boston, Massachusetts.

TABLE A

Mössbauer Transition Properties

For ^{119}Sn*

E_γ	gamma-ray energy	23.9 keV
$t_{1/2}(\gamma_M)$	half-life of Mössbauer transition	1.84×10^{-8} sec.
Γ	natural width	2.48×10^{-11} keV
Wo†	minimum observable width	0.62 mm sec^{-1}
Er	recoil energy	2.57×10^{-6} keV
I	nuclear spin quantum number for:	
	Ground state	1/2
	First excited state	3/2
$t_{1/2}$	half-life of Mössbauer Nucleide	250 days

Energy Conversion Factor   1 mm sec^{-1} = 7.96 x 10^{-8} eV

* A.H. Muir, K.J. Ando, and H.M. Coogan
 Mössbauer Effect Data Index, 1958-1965,
 Interscience Publishers, N.Y. 1966.

† Wo Equals Twice the Natural Line Width (2Γ)
 Because of Overlap of Emission and Absorption
 Lines.

a dewar of liquid nitrogen. After the absorber had been aligned with the source it was insulated with styrofoam to minimize heat transfer between the sample and the room. An automatic liquid nitrogen controller maintained the sample at 80° ± 1°K.

Mössbauer

(iii) Instrumentation*

The Mössbauer spectrometer which was used for this experimental work was of the constant acceleration type and experiments were performed with transmission geometry. This consists of measuring the intensity of radiation passing through a resonance absorber (sample) as a function of the relative velocity between source and absorber. The basic components of a Mössbauer spectrometer are the electromechanical velocity transducer, the detector, the multichannel analyser (MCA) and the discriminator or single-channel analyser.

The electromechanical velocity transducer modulates the incident energy by moving the source back and forth. It is driven by a wave-form (saw-tooth) generator which varies the velocity linearly with time. The detector is a gas-filled (2 atm. $Xe-CH_4$) proportional counter. Output from the detector is a series of pulses which are amplified. Only those pulses which lie within a given energy range are shaped and stored in the MCA. This MCA had 400 storage spaces or channels.
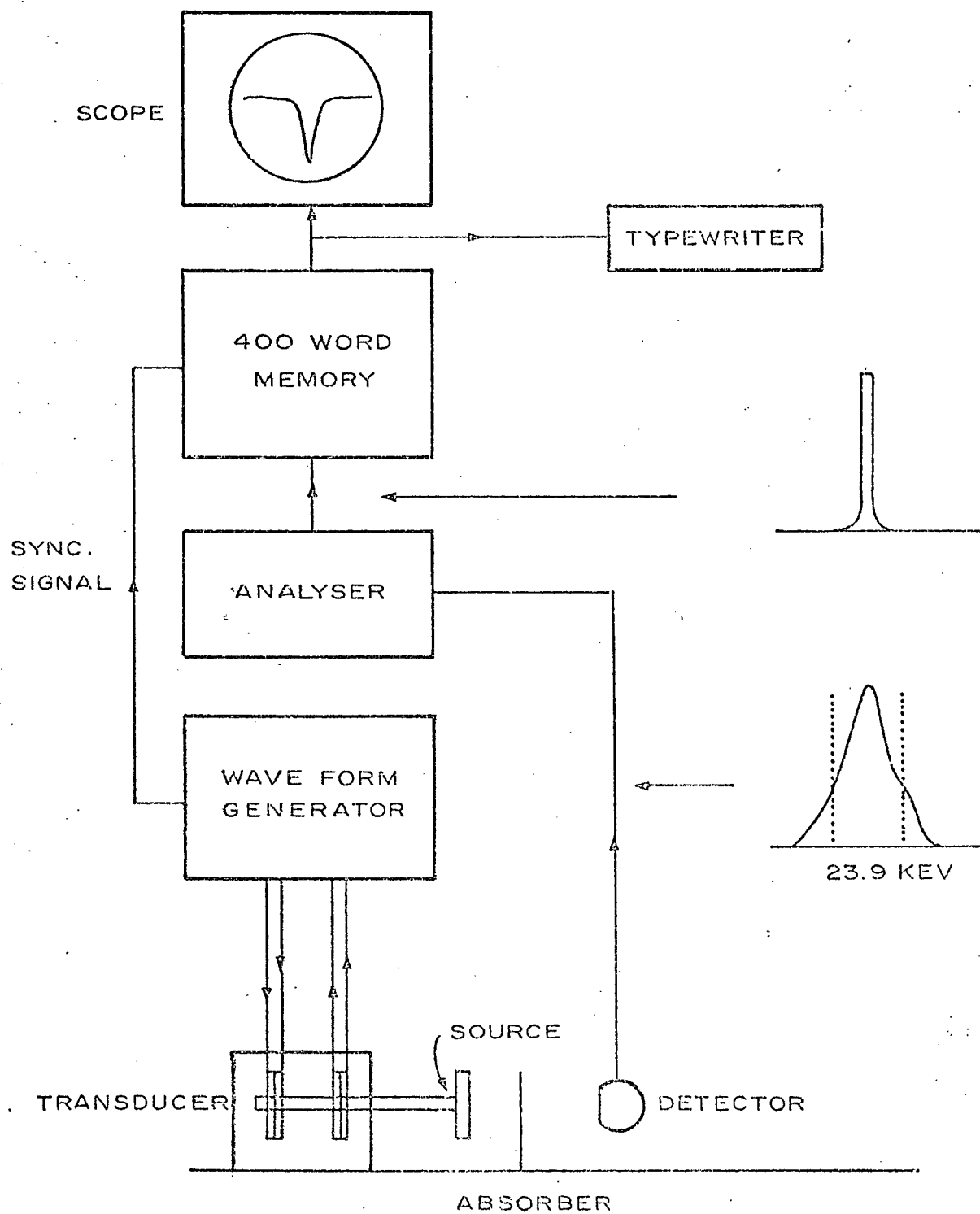
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* See FIGURE III

MÖSSBAUER SPECTROMETER

FIGURE III

The function of the discriminator is to select for storage only the Mössbauer gamma radiation. Before an absorption spectrum can be run a pulse-height spectrum (i.e. a spectrum of the radiation transmitted through the absorber) is obtained. A typical one is shown at the lower right in FIGURE III. The horizontal position of a peak is determined by its energy and the height by its relative intensity. The controls on the discriminator are adjusted to cut out all radiation except the Mössbauer line as shown by the dotted lines in the same FIGURE. Only that radiation falling within these limits is passed to the MCA for storage. Now an absorption spectrum can be run.

The Mössbauer spectrum consists of a record of counts versus channel number. Each of the 400 channels is made to correspond to a velocity increment in the velocity range being scanned and this is done as follows. At the start of each velocity cycle the wave-form generator sends a synchronization signal to the MCA to initiate sweep of its 400 channels. The rate (200 μsec per channel) of sweep is set so that equal time is spent counting in each channel. The velocity range is scanned repeatedly in this manner until sufficient data have been accumulated in the MCA. Final output is to an automatic typewriter which prints the number of counts in each channel. The channel address is converted to a velocity scale (mm sec^{-1}) by calibrating the instrument using the quadrupole splitting (1.726 ± 0.0002 mm sec^{-1}) of an N.B.S. standard sodium nitroprusside ($Na_2Fe(CN)_5NO.2H_2O$) absorber.

(iv) Treatment of Data and Errors

The spectrum consists of Mössbauer absorption peaks super-imposed on a parabolic background. A minimum number of 1.0×10^5 counts were accumulated in each channel before a spectral run was terminated. This meant that the statistical error did not exceed 0.3%.

The data along with estimates for the peak positions and line-widths (full width at half the maximum height) were substituted into a computer program* which performed a least squares fit of the data to a one or more Lorentizian line shapes.

The statistical scatter was low enough to enable an estimate of the error to be set on the basis of the standard deviation of the computer fit and the reproducibility of the spectrum. At least two spectra were run for each compound and it was found that the Mössbauer parameters, isomer shift and quadrupole splitting, were reproducible to within ± 0.03 mm sec^{-1}. An example of two fitted Mössbauer spectra is shown in FIGURE IV.

Infrared

Solid and solution infrared spectra were recorded on a Perkin-Elmer grating spectrometer (model 457) and were calibrated with poly-styrene. The solids were dispersed in nujol or halocarbon oil and each spectrum recorded from about 1800 to 250 cm^{-1} using cesium iodide windows.

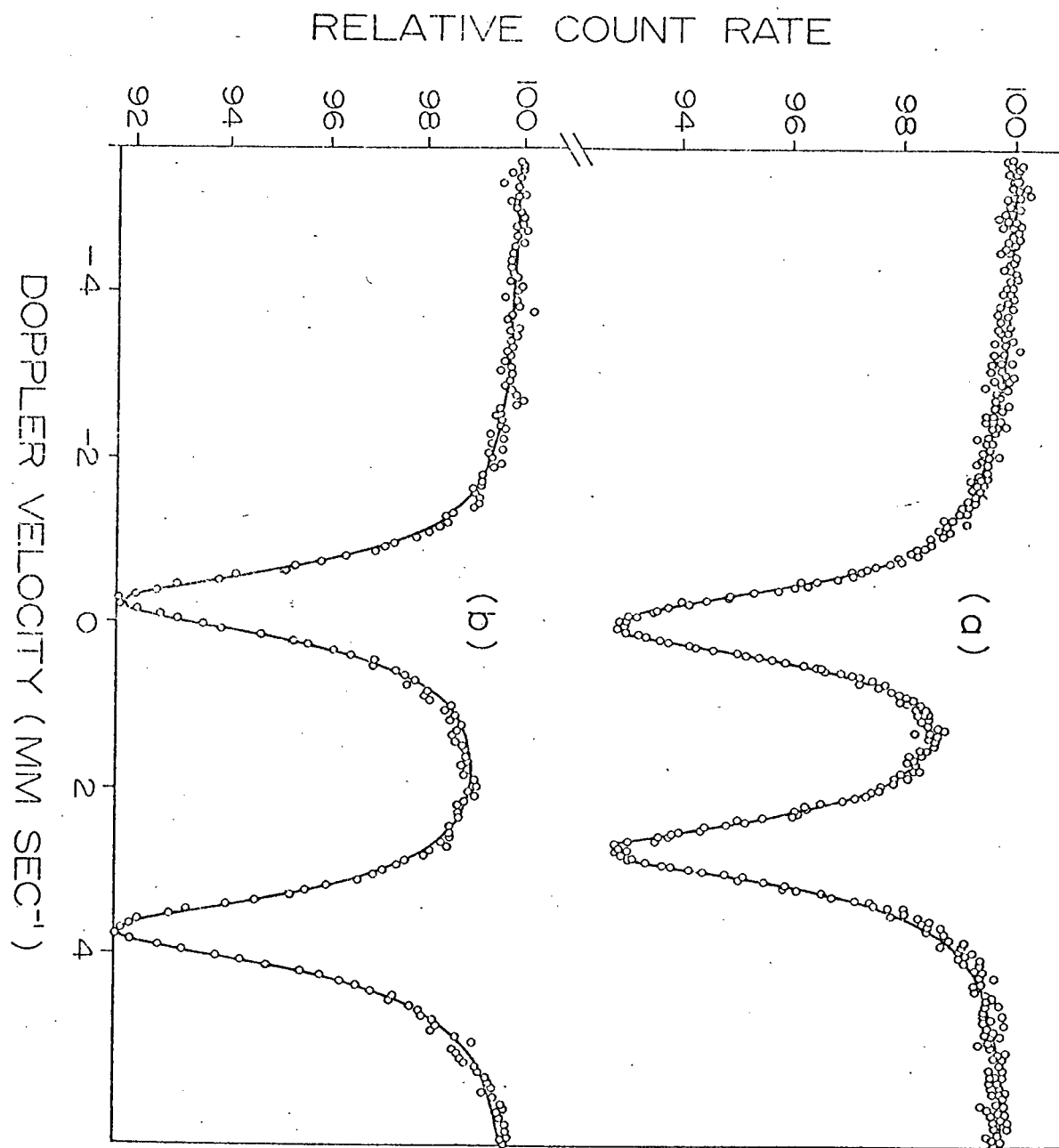* Written by the N.B.S. and subsequently modified by J.C. Scott.

FIGURE IV

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Dilute (3-5% by weight) carbon tetrachloride solutions were run using matched sodium chloride solution cells. Infrared data are in Tables IV - VI.

Preparations

Triphenyltin formate and triphenyltin propionate were prepared by shaking triphenyltin chloride with a slight excess of the sodium salt of the acid in an ether/water solvent system. The products were obtained from the ether layer and air dried. The remaining straight-chain carboxylates and the branched-chain carboxylates were prepared by reacting triphenyltin chloride with the potassium salt of the appropriate acid in methanol (reagent grade) at room temperature. Evaporation of the solvent left a white precipitate which was washed with water and air dried. Some of the products were purified further by recrystallization from carbon tetrachloride.

Triphenyltin monoiodoacetate was prepared in refluxing methanol by combining $\emptyset_3SnCl$ with the sodium salt of the acid.

The monobromo, monochloro, and dichloro derivatives were prepared by reacting triphenyltinhydroxide with a stoichoimetric amount of acid in methanol (reagent) at room temperature. The mixture was stirred from one to two hours then the solvent removed under reduced pressure and the products dried under the same conditions. When trichloroacetic acid was used the reaction produced $\emptyset_3SnOCOCCl_3 \cdot MeOH$ and pumping for several hours failed to remove the adducted methanol.

The trifluoro and trichloro derivatives were produced by reacting stoichiometric quantities of triphenyltinhydroxide and acid in ethanol (absolute) at room temperature. The solvent was removed under reduced pressure and the products dried in vacuo for a few days to remove "all" traces of ethanol.

Results

The compounds that were studied can be represented by the following formulation: $\emptyset_3^*SnOCOR$. The triphenyltin group, $\emptyset_3Sn$ is present in all compounds. Since the carboxylate group, OCOR, varies as the R group changes, only the chemical formulae for the R group is listed in the TABLES.

TABLES I - III contain analytical data and melting points, TABLES IV - VI contain infrared data, and TABLES VII - IX contain Mössbauer data.

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* $\emptyset$ = phenyl = C_6H_5

TABLE I

Analytical Data and Melting Points

R	%C		%H		m.p.
	calcd.	found	calcd.	found	°C
(1) H	57.72	57.86	4.05	4.01	201–202
(2) CH_3 [a]					121–124
(3) CH_2CH_3	59.57	59.63	4.73	4.91	122–123
(4) $(CH_2)_4CH_3$	61.93	60.39	5.59	5.46	110–111
(5) $(CH_2)_6CH_3$	63.28	63.51	6.09	6.13	81–83
(6) $(CH_2)_7CH_3$	63.90	64.25	6.31	6.29	106–107
(7) $(CH_2)_8CH_3$	64.49	64.22	6.53	6.53	80–82
(8) $(CH_2)_{10}CH_3$	65.57	65.37	6.92	6.93	76–78
(9) $(CH_2)_{14}CH_3$	67.43	67.48	7.60	7.79	77–80
(10) $(CH_2)_{16}CH_3$	68.25	68.67	7.90	8.35	71–73

[a] M & T Chemicals Inc.

TABLE II

Analytical Data and Melting Points

| R | %C | | %H | | m.p. |
	calcd.	found	calcd.	found	°C
(1) $(CH_2)_3CHMe_2$	62.63	62.32	5.85	5.76	93–96
(2) $(CH_2)_2CHMe_2$	62.06	62.08	5.60	5.89	102–105
(3) $CH_2CHMeEt$	62.06	62.33	5.60	5.76	110–112
(4) CH_2CHMe_2	61.19	61.27	5.32	5.52	103–105
(5) CHMePr	62.06	61.01	5.60	6.10	110–112
(6) $CHMe_2$	60.41	60.35	5.03	5.28	123–125
(7) $CH=CH_2$	59.86	59.72	4.28	4.36	150–151
(8) $CMe=CH_2$[a]					88–89
(9) CHE+Bu[a]					68–69
(10) CMe_3	61.19	60.94	5.32	5.27	103–105

[a] M & T Chemicals Inc.

TABLE III

Analytical Data and Melting Points

R	%C		%H		%X		m.p.
	calcd.	found	calcd.	found	calcd.	found	°C
(1) CH_2I	44.91	45.17	3.20	3.10	23.72	23.75	133-137
(2) CH_2Br	49.23	49.35	3.51	3.31	16.38	16.10	146-149
(3) CH_2Cl	54.16	54.38	3.72	3.66	7.99	8.21	154-156
(4) $CHCl_2$	50.26	50.08	3.37	3.20	14.83	14.60	174-177
(5) CCl_3	46.88	47.09	2.95	2.94	20.76	20.58	86-89
(6) CF_3	51.84	51.71	3.24	3.27	12.31	12.08	121-123
(7) $CCl_3 \cdot MeOH$	46.29	46.09	3.49	3.40	19.56	19.80	104-107

TABLE IV

Infrared Data

R	C-O Stretching Frequencies			
	Solid-State $(cm)^{-1}$		CCl_4 Solution $(cm)^{-1}$	
(1) H	1559	1390	1644	1358
(2) CH_3	1548	1420	1640	1370
(3) CH_2CH_3	1535	1412	1632	1381
(4) $(CH_2)_4CH_3$	1534	1407	1634	1381
(5) $(CH_2)_6CH_3$	1525	1415	1631	1382
(6) $(CH_2)_7CH_3$	1525	1409	1628	1368
(7) $(CH_2)_8CH_3$	1532	1404	1630	1382
(8) $(CH_2)_{10}CH_3$	1531	1406	1628	1380
(9) $(CH_2)_{14}CH_3$	1530	1408	1630	1381
(10) $(CH_2)_{16}CH_3$	1532	1410	1629	1380

TABLE V

Infrared Data

R	C-0 Stretching Frequencies			
	Solid-State (cm)$^{-1}$		CCl$_4$ Solution (cm)$^{-1}$	
(1) $(CH_2)_3CHMe_2$	1529	1416	1631	1387
(2) $(CH_2)_2CHMe_2$	1533	1404	1629	1388
(3) $CH_2CHMeEt$	1524	1407	1628	1382
(4) CH_2CHMe_2	1523	1408	1643	1380
(5) CHMePr	1536	1416	1638	1379
(6) $CHMe_2$	1533	1422	1632	1391
(7) $CH=CH_2$	1528	1423	1619	1335
(8) $CMe=CH_2$	1595	1345	1610	1360
(9) CHE+Bu	1630	1336	1625	1340
(10) CMe_3	1622	1330	1624	1332

TABLE VI

Infrared Data

R	C-0 Stretching Frequencies			
	Solid-State $(cm)^{-1}$		CCl_4 Solution $(cm)^{-1}$	
(1) CH_2I	1548	1380	1650	1324
(2) CH_2Br	1568	1409	1686	1353
(3) CH_2Cl	1576	1411	1663	1345
(4) $CHCl_2$	1595	1402	1683	1330
(5) CCl_3	1655	1340	1705	1296
(6) CF_3	1650	1447	1722	1400
(7) $CCl_3 \cdot MeOH$	1665	1334	1702	1294

TABLE VII

Mossbauer Data at 80°K.

R	$\delta^{a,b}$ (mm. sec^{-1})	Δ^a (mm. sec^{-1})	Γ_1^a (mm. sec^{-1})	Γ_2^a
(1) H	1.37	3.58	0.85	0.87
(2) CH_3	1.27	3.40	0.77	0.77
(3) CH_2CH_3	1.33	3.42	0.99	1.01
(4) $(CH_2)_4CH_3$	1.32	3.43	0.98	1.00
(5) $(CH_2)_6CH_3$	1.29	3.35	1.03	1.11
(6) $(CH_2)_7CH_3$	1.28	3.36	1.03	1.17
(7) $(CH_2)_8CH_3$	1.27	3.46	0.96	0.98
(8) $(CH_2)_{10}CH_3$	1.24	3.41	0.97	1.07
(9) $(CH_2)_{14}CH_3$	1.25	3.44	0.94	0.97
(10) $(CH_2)_{16}CH_3$	1.26	3.33	0.98	1.06

a
± 0.03 mm. sec^{-1}

b
relative to SnO_2 at 80°K

TABLE VIII

Mossbauer Data at 80°K.

R	$\delta^{a,b}$ (mm. sec^{-1})	Δ^a (mm. sec^{-1})	Γ_1^a (mm. sec^{-1})	Γ_2^a
(1) $(CH_2)_3CHMe_2$	1.25	3.36	0.98	1.01
(2) $(CH_2)_2CHMe_2$	1.26	3.38	0.97	0.97
(3) $CH_2CHMeEt$	1.29	3.39	1.02	1.03
(4) CH_2CHMe_2	1.27	3.39	1.02	0.94
(5) $CHMePr$	1.26	3.34	0.98	1.05
(6) $CHMe_2$	1.28	3.32	0.95	1.07
(7) $CH=CH_2$	1.28	3.41	0.87	0.95
(8) $CMe=CH_2$	1.21	2.26	0.90	0.93
(9) $CHE+BU$	1.21	2.26	0.97	1.02
(10) CMe_3	1.21	2.40	0.93	0.99

a
± 0.03 mm. sec.$^{-1}$

b
relative to SnO_2 at 80°K.

TABLE IX

Mossbauer Data at 80°K.

| R	$\delta^{a,b}$ (mm. sec^{-1})	Δ^a (mm. sec^{-1})	Γ_1^a (mm. sec.$^{-1}$)	Γ_2^a
(1) CH_2I	1.31	3.59	0.71	0.75
(2) CH_2Br	1.32	3.51	0.90	0.96
(3) CH_2Cl	1.32	3.53	1.00	1.00
(4) $CHCl_2$	1.35	3.81	0.97	0.92
(5) CCl_3	1.37	3.75	1.08	1.11
(6) CF_3	1.40	4.00	0.92	0.97
(7) $CCl_3 \cdot MeOH$	1.33	3.50	0.87	0.94

a ± 0.03 mm. sec.$^{-1}$

b relative to SnO_2 at 80°K.

DISCUSSION

Preparations

Most of the preparations were simple to carry through and products were obtained in high yields (~80%). Difficulties arose when the following preparative method:

$$\emptyset_3SnCl + Na \text{ salt of acid} \xrightarrow{MeOH}$$
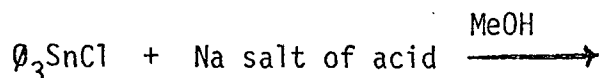
was tried for the halogen-substituted acids. The reaction was carried out at room temperature and at the temperature of refluxing methanol but was not successful in giving a quantitative yield of major product. Either no reaction occurred or there were side reactions which gave a mixture of products. Only $\emptyset_3SnOCOCH_2I$ was prepared using the above method.

An alternate route was to use triphenyltin hydroxide and the acid as starting materials. Methanol was kept as the solvent. After several attempts during which the temperature and amount of starting material was varied, the monobromo, monochloro and dichloro derivatives were made. However similar reaction conditions (stoichiometric amounts of triphenyltin hydroxide and trichloroacetic acid or trifluoroacetic acid in methanol at room temperature) failed to produce the corresponding trichloroacetate and trifluoroacetate derivatives. When trichloroacetic acid was used in the preparation, the white solid which remained after the methanol was pumped off turned out to be a |:| methanol adduct of $\emptyset_3SnOCOCCl_3$. However a similar addition compound was not isolated for the trifluoroacetate derivative. After several hours of pumping a viscous

liquid still remained in the reaction vessel. The reaction solvent was changed from methanol to absolute ethanol. It seemed reasonable that ethanol would not form an addition compound with the trichloroacetate derivative as easily as methanol. Both starting materials (triphenyltin hydroxide and trichloroacetic acid or trifluoroacetic acid) were still as readily soluble in the new solvent and each reaction was carried out at room temperature. The desired products were eventually isolated.

When an excess of trifluoroacetic or trichloroacetic acid was used or the reaction was carried out under refluxing conditions a mixture of products was obtained (the Mössbauer spectrum showed four or more lines). Although no attempt was made to separate this mixture it is possible to infer what other compounds are likely to have been produced. Recently a number of triphenyltin carboxylates were prepared [15]. Triphenyltin acetate, propionate, chloroacetate, and isobutyrate were synthesized by the following method:

$$\emptyset_3 SnOH + acid \xrightarrow[\text{reflux}]{\text{anhydrous benzene}}$$
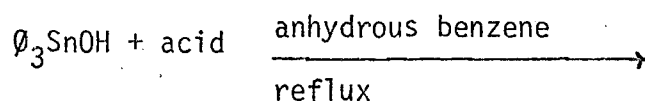
Attempts to make triphenyltin trifluoroacetate and trichloroacetate gave insoluble phenylstannoxane carboxylates $\emptyset Sn(O)OCOR$ (R = CF_3 and CCl_3) which all had m.p. >360°. It is likely that our "mixture of products" contained some triphenyltin carboxylate, some of the final product or phenylstannoxane carboxylate and possibly some of the intermediate product, a phenyltin tricarboxylate which is subsequently hydrolysed to the final product.

Infrared

(i) Introduction

The carboxylate group can be characterized by two absorption bands in the infrared region. The band positions (cm^{-1}) depend on the chemical nature of this group. For example organic esters absorb at about 1740 and 1240 cm^{-1} and salts of organic acids absorb between 1610-1550 cm^{-1} and 1400-1300 cm^{-1}.[16]

The higher energy absorption is referred to in the literature as a carbonyl band or an asymmetric stretching vibration and the lower energy absorption is called a carboxyl band or a symmetric stretching vibration. In the experimental results (TABLES IV - VI) the bands are referred to as c-o stretching frequencies.

Several authors[1-3] have observed that the band positions for the solid state spectra of several trialkyltin carboxylates differ significantly from the band positions for dilute solution spectra of the same compounds. For example van der Kerk et al.[1] report solid state bands at about 1570 and 1410 cm^{-1} and solution bands at about 1650 and 1300 cm^{-1} for a number of trialkyltin carboxylates, $R_3SnOCOR'$

(R=methyl, ethyl, butyl, hexyl and R'=methyl,
R=methyl and R'=dodecyl)

The solid state bands are similar to those of a salt-like or bridging carboxylate while the positions of the solution bands are

much closer to those for an organic ester. From these observations

the following conclusion was made about the structure of the compounds.

The solid is a polymeric compound having a pentacoordinate Sn atom and in

a dilute solution it becomes a monomer having a tetracoordinate Sn atom.

The absorption energies for triorganotin carboxylates differ

significantly from those previously quoted (first paragraph, last sentence

of this section). The author's suggest that this difference can be

attributed to the presence of a heavy metal atom which influences the

c-o vibrations in the molecule. This seems reasonable however it would

be difficult to separate the mass effect from electronic effects which

could also shift the absorption energy.

(ii) Experimental Results

Only <u>three</u> compounds have the same (small differences can be

attributed to solvent effects) c-o stretching frequencies for the solid

and solution. These are in the branched series (TABLE IV, compounds

8,9, and 10) and are: triphenyltin methacrylate,triphenyltin 2-ethylhexanoate

and triphenyltin trimethylacetate. The band positions indicate that the

compounds are monomeric in the solid state and in solution. This implies

a tetracoordinate Sn atom.

All the other compounds in the branched series (TABLE V) and

all the compounds in the linear series (TABLE IV) have c-o stretching

frequencies for the solid which are at approximately 1530 and 1410 cm^{-1}.

The c-o stretching frequencies for a dilute CCl_4 solution of the same

compounds are at 1630 and 1380 cm^{-1}. These results indicate that the

compounds are polymeric in the solid and monomeric in solution.

For several of the pentacoordinate compounds it was observed that if the concentration of the solution was increased there appeared two low intensity bands where absorption normally occurs for the same compound in the solid state. This is evidence for association and lends support to a solid state structure which is polymeric rather than ionic. The fact that the solids are soluble in non-polar solvents also indicates that they are not ionic.

The haloacetates (TABLE VI) show a larger difference between c-o stretching frequencies for different compounds within the series and therefore averaging the band positions wouldn't be very meaningful. However after comparing the solid and solution c-o bands for each haloacetate it is evident that the compounds are polymeric in the solid and monomeric in solution.

The haloacetates have been arranged in the TABLES in order of increasing acid strength (for the parent acid) going down the series and there appears to be a trend. As the acid strength increases there is a larger separation between c-o bands for both the solid and solution. In other words the band positions move closer to those for an organic ester as the acid strength increases. The pK values for the parent acid range from about 3 for monoiodoacetic acid to <1 for trichloro- and trifluoroacetic acid.

There doesn't appear to be any similar trends in the c-o stretching frequencies for the pentacoordinate linear and branched non-halogenated

carboxylates. All the parent acids are weak and the pK values fall in a narrow range, pK ~ 4-5.

Mössbauer

(i) Introduction

The usefulness of Mössbauer spectroscopy in studying the structures of triorganotin carboxylates depends on a comparison of data for unknown samples with that derived from model compounds. For these studies it would be necessary to know the isomer shift and quadrupole splitting data for a few triorganotin carboxylates with a pentacoordinate and a tetracoordinate Sn atom.

It has been fairly well established from infrared studies that trimethytin acetate and tri(n)butyltin acetate are polymeric in the solid and therefore have pentacoordinate Sn atoms. Recently an x-ray analysis of the crystal structure of trimethyltin acetate has confirmed that it is polymeric.[17]

We have recorded Mössbauer data for these two compounds:

	δ(mm sec^{-1})	Δ(mm sec^{-1})
trimethyltin acetate	1.35	3.68
tributyltin acetate	1.45	3.64

The results are very similar. The isomer shifts are in the range for Sn(IV) compounds and the quadrupole splitting values are reasonably high (3.6 - 3.7 mm sec^{-1}).

Model compounds in which the Sn atom is very probably tetra-

coordinate are derivatives of tetraneophyltin. The neophyl group

$$Me - \underset{\underset{\emptyset}{\overset{\displaystyle Me}{|}}}{C} - CH_2 -$$
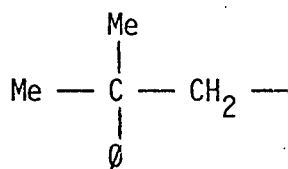
is a bulky substituent and consequently it has been postulated[12] that trineophyltin chloride and trineophyltin acetate have a tetracoordinate Sn atom. Also, chemical reactions involving tetra-neophyltin and trineophyltin chloride are inhibited and this has been attributed to the effect of a sterically hindered Sn atom[18].

	δ(mm sec^{-1})	Δ(mm sec^{-1})	
(neophyl)$_4$Sn	1.34	0	
	1.21	0	$\emptyset_4$Sn
(neophyl)$_3$SnCl	1.39	2.65	
	1.37	2.45	$\emptyset_3$SnCl
(neophyl)$_3$SnOCOCH$_3$	1.35	2.45	
	1.27	3.40	$\emptyset_3$SnOCOCH$_3$

All values are from reference 12 except for triphenyltin acetate which is ours. The Mössbauer parameters for the corresponding phenyl compounds are included for comparison.

From the previous discussion it is now expected that both tetra-and pentacoordinate triphenyltin carboxylates will show quadrupole splitting, however the magnitude of the splitting will be different for each structural type and lower ($\sim$1.0 mm sec^{-1}) for the tetracoordinate compound which has $\Delta \sim$2.5 mm sec^{-1}. The isomer shift values are indicative of Sn(IV) compounds and they differ slightly ($\sim$.1 mm sec^{-1}) as the organic groups and more electronegative groups on Sn are changed.

(ii) Experimental Results

Three compounds (TABLE VIII, compounds 8,9 and 10) have quadrupole

splitting values which are significantly lower (1.0-1.7 mm sec^{-1}) than

for all other compounds listed in the TABLES. The magnitude of the

quadrupole splitting (~2.3 mm sec^{-1}) is similar to that for the tri-

neophyltin compounds (Δ~2.5 mm sec^{-1}). From these observations tri-

phenyltin 2-ethylhexanoate, triphenyltin methacrylate and triphenyltin

trimethylacetate are postulated to have tetracoordinate Sn atoms. All

the other compounds have quadrupole splitting values which are indicative

of a pentacoordinate Sn atom (Δ ranges from 3.3-4.0). FIGURE IV, page 18,

shows the Mössbauer spectrum for a monomeric compound, (a) triphenyltin

methacrylate, and a polymeric compound, (b) triphenyltin acrylate. The

difference in quadrupole splitting is quite marked.

The larger values for the quadrupole splitting of the polymeric

compounds can be explained by an increased asymmetry in 5p-electron

charge, assuming no contribution from non-bonding closed shells and

5 s-electron charge because of their spherical symmetry. The asymmetry

in 5p-electron charge could occur as a result of the change in valence

electron distribution as the structural type changes from a distorted

tetrahedron for the monomeric compounds to a trigonal bipyramid for the

polymeric compounds. The largest quadrupole splitting values are found

for the haloacetates, TABLE IX. Since these compounds have more electro-

negative substituents on the α-carbon atom it is likely that this further

distorts (indirectly via the c-o groups) 5p-electron distribution.

The isomer shift values for the compounds studied are the same magnitude as other Sn(IV) compounds ($\delta \sim 1.2 - 1.3$ mm sec^{-1}). Within a given series the δ values for some of the compounds differ by as much as .1 mm sec^{-1}. It is speculative whether this is significant, however in some instances there appear to be plausible reasons and some of these will be mentioned.

The δ values are consistently higher for the polymeric solids (all compounds in TABLES VII - IX except 8,9 and 10 in TABLE VIII). This means there is a slight increase in s-electron density at the Sn nucleus and can be explained by a decrease in shielding of 5 s-electron charge by 5 p-electron charge. This is reasonable since a change in the distribution of valence electron charge (mainly 5s and 5p) is expected for a change in bonding from a tetracoordinate to a pentacoordinate Sn atom. However it might have been difficult to predict the relative electron density changes without the Mössbauer results.

The δ values for the haloacetates are slightly higher than for the non-haloacetates which are also polymeric. Apparently there is further deshielding of s-electron charge and indirectly this could be due to more electronegative substituents on the α-carbon atom. One might therefore expect R=CF$_3$ to have a higher isomer shift than R=CH$_2$I and this is observed. There is also a small increase in isomer shift down the series which is arranged in order of increasing acid strength for the parent acid, HOCOR.

The Mössbauer results in TABLE VII show no correlation be-
tween the length of the R group and the isomer shift or quadrupole
splitting. Similar conclusions can be made for the compounds
containing branching groups (excluding the three monomeric compounds,
TABLE VIII compounds 8,9 and 10)

Structure and Bonding

Lengthening the hydrocarbon group, R, to 18 carbon atoms
doesn't inhibit polymer formation in triphenyltin carboxylates. Methyl
branches at the 2-5 carbon atom positions also do not prevent polymer
formation. However an ethyl and a butyl branch or three methyl groups
at the α-carbon atom are sufficiently bulky to give a monomeric solid
state structure.

One might have expected triphenyltin methacrylate, which has
a methyl and a methylene group on the α-carbon atom, to be polymeric
like triphenyltin isobutyrate which has two methyl groups and a hydrogen
atom bonded to the α-carbon atom. The methylene group is about as bulky as
a methyl group (van der Waals radius for both ~ 2.0 A°). A likely
explanation is that for the methacrylate the α-carbon forms sp^2-hybridized
bonds and therefore the three atoms bonded to it will be close to a
trigonal planar arrangement in contradistinction to the isobutyrate
in which the α-carbon atom is in a tetrahedral environment. The methacrylate
group is now restricted in its orientation capabilities and consequently
interacts to sterically hinder polymer formation.

In view of the previous discussion it is informative to compare the experimental results for triphenyltin acrylate with that for triphenyltin methacrylate. The existence of different structures for these compounds is evident from their Mössbauer spectra shown in FIGURE IV. Triphenyltin acrylate is designated as (b) in the Figure. In triphenyltin acrylate the three groups or atoms bonded to the α-carbon atom will again be nearly coplanar. However the replacement of a methyl group by a H atom makes the carboxylate group less bulky and consequently the compound is polymeric.

Halogen atoms bonded to the α-carbon atom do not prevent polymer formation. Even three Cl atoms, where each Cl atom has a van der Waals radius (1.80 A°) very close to that for a methyl group (2.0 A°), do not produce the same structural change in the solid as three methyl groups.

THEORETICAL DISCUSSION

Point-Charge Predictions of Quadrupole Splitting Values

A point-charge model[6-8] can be used to predict quadrupole splitting Δ values for the triphenyltin haloacetates from Δ values for the corresponding trimethyltin derivatives which are isostructural compounds.[5]

The quadrupole splitting is given by

$$\Delta = 1/2\ eQVzz\ (1 + \eta^2/3)^{1/2}$$

where eQ is the nuclear quadrupole moment, $\eta = (V_{xx} - V_{yy})/V_{zz}$, and the V_{ii} are the diagonal electric field gradient, efg, tensor elements. By convention the axes are chosen so that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$.

The electric field gradient which gives rise to the quadrupole splitting is due both to charges on the ligands and surrounding atoms or ions ($q_{LATTICE}$) and to imbalances in the distribution of the valence-shell electrons on the Sn atom ($q_{VALENCE}$). It has recently been shown[18] that $q_{VALENCE}$ dominates the splitting.

In the point-charge model the ligands, L, are considered as localizations of electronic charge, q_L, situated at a distance r_L from the central metal atom. The contribution [L] of a particular ligand to the efg is given by

$$[L] = <q_L r_L^{-3}>$$

The [L] is used strictly as an empirical parameter in our calculations.

An expression for Δ in terms of [L] can be obtained for a

molecule of the type R_3SnX_2 which has trigonal bipyramidal symmetry about the Sn atom. This is an ideal structural type which is approximated by the polymeric triphenyltin carboxylates, FIGURE I.

Choosing the z-axis along the O-Sn-O direction gives $\eta = 0$ because of axial symmetry i.e. the x and y contributions to the efg are equal. The only contribution comes from V_{zz} which can be written as:

$$V_{zz} = \sum_L [L] (3 \cos^2 \theta_L - 1)$$

Substituting [R] and [X] for [L] gives

$$\Delta = 4[X] - 3[R]$$

where the factor 1/2 eQ has been incorporated into the parameter [L]. [L] has been referred to as a partial quadrupole splitting, PQS, parameter[19].

Parish and Platt[7] have estimated PQS values for a number of substituents (all the compounds contain a pentacoordinate Sn atom). Using their values for [Me] and [Ph] and the Δ values for the tri-methyltin haloacetates[5] it is possible to predict Δ values (Δ') for the triphenyltin haloacetates.

$$\Delta = 4[X] - 3[Me]$$
$$\Delta' = 4[X] - 3[Ph]$$
$$\Delta' = \Delta + 3 ([Me] - [Ph])$$

The Δ_{PRED} values agree quite well (within .1 mm sec^{-1}) with the $\Delta_{OBS.}$ values. It is important to note that the difference

[Me] - [Ph] is required in the computation and not the actual values for [Me] and [Ph].

This theoretical model of quadrupole interactions assumes that equivalents of charge are transferable and it appears to have a fair predictive accuracy when applied to homologous series.

TABLE X

Point-Charge Predicted Quadrupole
Splitting Values for Triphenyltin Haloacetates

R	$\Delta_{OBS.}$ (mm sec^{-1})	$\Delta_{PRED.}$ (mm sec^{-1})
(1) CH_3	3.40	3.35
(2) CH_2I	3.59	3.50
(3) CH_2Br	3.51	3.57
(4) CH_2Cl	3.53	3.56
(5) $CHCl_2$	3.81	3.75
(6) CCl_3	3.75	3.82
(7) CF_3	4.00	3.89

CONCLUSION

In general triphenyltin carboxylates are polymeric in the solid-state and have bridging carboxylate groups and pentacoordinate Sn atoms. Three of the compounds studied were found to be monomeric solids. It was concluded that the structural change from a polymeric to a monomeric solid could be attributed to steric interaction between substituents on the α-carbon atom and neighbouring phenyl groups bonded to Sn.

An attempt was made to determine the minimum size of substituent (tri-substituted at the α-carbon atom) which would result in a monomeric compound. Three methyl groups (van der Waals radius ~2.0A°) give a monomeric compound but three chlorine groups (van der Waals radius ~1.8A°) give a polymeric compound. Apparently the "critical" size is between 1.8 and 2.0A°.

The most unexpected result was the existence of an addition compound of triphenyltin trichloroacetate,$\emptyset_3SnOCOCCl_3 \cdot MeOH$. The Mössbauer and infrared data indicate that the compound is a polymer with bridging carboxylate groups. As a rule Sn (organotin) has a tendency to increase its coordination number from four to five or six[20], consequently it is common to find addition compounds formed from electron donor solvents. To my knowledge this is the first adduct of a tri-organotin carboxylate that has been reported.

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