

COORDINATION CHEMISTRY OF THE DIMETHYLTIN MOIETY

by

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A dissertation submitted to the
Graduate Faculty in Chemistry in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy,
The City University of New York

1970

This manuscript has been read and accepted
for the Graduate Faculty in Chemistry in
satisfaction of the dissertation requirement
for the degree of Doctor of Philosophy.

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ACKNOWLEDGMENT

I wish to express my deepest appreciation to The City University of New York and the Department of Chemistry, Brooklyn College for financial assistance; to M & T Chemicals, Inc. for kindly donating chemicals; to Ivor Simmons of M & T Chemicals, Inc. for performing the molecular weight measurements; to Professor Leopold May, The Catholic University of America, Washington, D. C., for performing the Mössbauer spectra; to Professor Harmon Finston, George Bing and David Berne for advice and assistance in constructing the figures; to my fellow graduate students for many helpful discussions; to Mrs. Helen Feldman whose skillful typing was instrumental in turning this manuscript into a polished dissertation.

I would like to acknowledge the helpful guidance of Professor Clyde R. Dillard. It has been intellectually stimulating as well as a distinct pleasure working with him.

To my parents, Mr. & Mrs. S. B. Cohen, I wish to express my profound gratitude for moral, spiritual, and financial assistance throughout my entire graduate school career.

Last but not least I want to thank my wife, Pnina, for her patience, encouragement, and understanding during my doctoral studies. I want to ask her forgiveness for spending many lonely nights and Sundays while I worked in the laboratory.

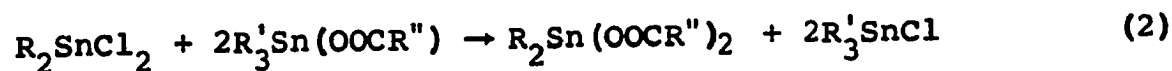
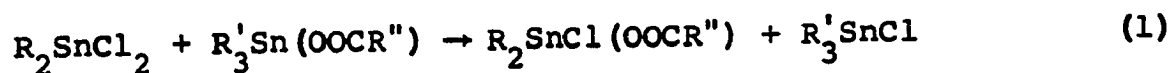
Abstract

A homologous series of dimethyltin bis (p-substituted benzoates) in which the para-substituent is varied have been studied by means of infrared, H^1 nuclear magnetic resonance, and Sn^{119m} Mössbauer spectroscopies. The existence of a Mössbauer effect at room temperature and molecular weights which increase with increasing concentration has been interpreted as arising from the polymeric nature of these compounds in the solid state, involving bridging carboxyl groups. Molecular weight studies suggested monomeric structures in dilute solution with the carboxyl groups being internally chelating.

In nuclear magnetic resonance studies it was found that the chemical shift, τ ($Sn-CH_3$), of these compounds in solution was identical. On the other hand, Mössbauer effect studies at $77^\circ K$ indicated that the para-substituent influences the total electron density around the tin atom since the isomer shift, δ_o , was found to vary in an almost linear fashion with the donor properties of these substituents. This was taken as evidence that in the series of compounds, the polarity of the tin-oxygen bonds varies over a considerable range.

By use of infrared spectroscopy the separation of the asymmetric and symmetric COO stretching vibrations in the solid were compared with the analogous separation of the corresponding sodium carboxylates. Ratios of 1.05 - 1.33 were found. Our interpretation of these data was that such a range corresponds to bridging carboxyl groups since a range of 0.94 - 1.32 was found for triorganotin carboxylates known by x-ray studies to be polymeric with bridging carboxyl groups. Infrared studies of the dimethyltin bis (p-substituted benzoates) in solution, compared with the analogous salts, yielded ratios ranging from 1.38 - 1.61, which, in view of the monomeric nature of these compounds, is considered to correspond to internally chelating carboxyl groups. It was proposed that such an approach would be useful in ascertaining the mode of coordination of other non-transition-metal carboxylates.

The reactions of organotin halides with organotin carboxylates were studied. It was found that diorganotin dihalides react with triorganotin carboxylates according to the following equations:



where R and R' = CH₃ or C₆H₅; and R'' = CH₃, ClCH₂, or C₆H₅. In addition, diorganotin halide carboxylates were found to react with triorganotin carboxylates in a 1:1 mole ratio to yield R₂Sn(OOCR'')₂, indicating that reaction (2) proceeds in a stepwise manner. The course of the reactions were followed by use of nuclear magnetic resonance techniques as well as by isolation of the products. These reactions permitted the preparation of compounds, such as (C₆H₅)₂SnCl(OOCC₆H₅), which have not been prepared using other synthetic methods. Possible mechanisms were discussed. The available evidence suggested that reaction (1) involves a Lewis acid--Lewis base type of attack on diorganotin dihalide by the free carbonyl of R'₃Sn(OOCR'') forming an intermediate whereby the coordination of both tin atoms is expanded to five.

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INTRODUCTION

The chemistry of organotin compounds has been the subject of considerable interest in recent years.^{1,2} Tin is a versatile element forming a variety of organic derivatives such as $\text{Sn}(\text{OOCH})_2$,³ $(\text{CH}_3)_2\text{SnCl}_2$,¹ $(\text{CH}_3)_3\text{SnCl}$, pyridine,⁴ $(\text{alkyl})_2\text{Sn}(\text{OOPR}_2)_2$,⁵ and $\text{C}_6\text{H}_5\text{Sn}(\text{tropolonate})_3$,⁶ having a coordination number around tin of two, four, five, six and seven, respectively. Methyltin compounds have been most extensively studied because of the structural inferences readily made on the basis of infrared and NMR spectroscopy (vide infra). Of particular interest are the organotin carboxylates because the nature of the bonding in these compounds appears to depend on their physical state. For example, in the solid, trialkyltin carboxylates have bridging COO groups with five-coordinate tin. However, in dilute solution a free-ester with four-coordinate tin is the predominant species.⁷

This investigation was undertaken with the following objectives: (a) to delineate the extent to which the dimethyltin moiety, $(\text{CH}_3)_2\text{Sn}$, may be used as a probe in making structural assignments of organotin chelates; (b) to correlate the results of Mössbauer spectroscopy with the nature of the tin-oxygen bond as well as with the

stereochemistry for compounds of the type $(p\text{-XC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$, ($\text{X} = \text{H}, \text{Cl}, \text{CN}, \text{NO}_2, \text{NH}_2, \text{CH}_3, \text{CH}_3\text{O}$); (c) to establish criteria from infrared spectroscopy for distinguishing between bridging and internally chelating carboxyl groups in organotin carboxylates; (d) to isolate five-coordinate organotin compounds such as $\text{R}_2\text{SnCl}(\text{OOCR}')$ and study the influence of R and R' on their stability; (e) to study the exchange and redistribution reactions of organotin chelates and organotin dihalides. •

The investigations reported in this work have made the following contributions to the chemistry of organotin compounds:

(1) The reliability of the dimethyltin moiety as a probe for the determination of structure of organotin compounds has been evaluated.

(2) The study of a homologous series of dimethyltin bis (p -substituted benzoates) has tested both the consequences of subtle electronic effects on the structures of organotin chelates and the extent to which the π -system of the benzene ring influences the properties of these compounds.

(3) This investigation has provided some insight into the reasons for differences already noted⁸ in the properties of organotin carboxylates of aliphatic acids and organotin carboxylates of aromatic acids.

(4) New types of five-coordinate diorganotin halide carboxylates have been isolated.

(5) New synthetic routes to diorganotin bis (carboxylates) and diorganotin halide carboxylates through the reaction of diorganotin dihalides with triorganotin carboxylates were developed.

(6) The isolation of five-coordinate intermediates in these exchange reactions afforded the opportunity to study the mechanism of formation of five-coordinate diorganotin halide carboxylates and their disproportionation in solution into four- and six-coordinate organotin carboxylates.

CHAPTER I

LITERATURE SURVEY

This chapter will survey the reported methods of determining the structure of organotin chelates with special emphasis on dimethyltin compounds. Also, reports on the exchange and redistribution reactions involving methyltin halides and organotin chelates will be reviewed.

A. Survey of Structural Methods.

The tool which provides the most complete picture of the structure of organotin compounds is three-dimensional x-ray diffraction. It has been applied to the study of the adduct of pyridine with trimethyltin chloride,⁴ to trimethyltin cyanide,⁹ to dimethyltin difluoride,¹⁰ to dimethyltin bis (8-hydroxyquinolate),¹¹ and to $[(CH_3)_2 SnCl, \text{terpyridyl}] [(CH_3)_2 SnCl_3]$.¹² Thus far, only these few studies have been reported. In addition x-ray studies do not provide information on structures in solution. In this thesis, therefore, x-ray diffraction will not be further discussed.

Nuclear magnetic resonance, Mössbauer, and infrared spectroscopy have been more widely applied in studying the structures of organotin compounds. The advantages and

limitations of these methods in applications to the chemistry of dimethyltin chelates will now be discussed.

1) Nuclear Magnetic Resonance Spectroscopy.

When a nucleus with a magnetic moment is placed in an external magnetic field, the interaction of the magnetic moment with the external field produces a torque. The classical interaction of the torque with the angular momentum causes the magnetic moment to precess about the external field.¹³ The angular frequency of this precession, called the Larmour frequency is given by Equation 1,

$$\omega = \gamma H_0 \quad (1)$$

where, ω is the Larmour frequency, H_0 is the applied field strength, and γ is the gyromagnetic ratio.⁷ In the more common NMR experiment one varies the field strength until ω becomes equal to a fixed applied frequency, such as 60 or 100 MHz.

A NMR spectrum, usually run neat or in solution, generally supplies information concerning the chemical shift, τ , and the fine structure, referred to as spin-spin coupling. The chemical shift is defined¹³ as

$$\tau = 10 + \delta \quad (2)$$

where δ is the difference in shielding constants of the sample and reference compound (usually tetramethylsilane).¹³ Spin-spin coupling arises¹³ from the various possible combinations of nuclear magnetic moments of those nuclei present in the compound with a nuclear spin quantum number, $I = \frac{1}{2}$. Examples of such nuclei are ^1H , ^{31}P , ^{19}F , ^{117}Sn , ^{119}Sn , etc.

For methyltin compounds NMR spectroscopy yields the chemical shift, τ , of the protons of the Sn-CH_3 group as well as the tin-methyl proton coupling constants, $J(^{117}\text{Sn-C-H})$ and $J(^{119}\text{Sn-C-H})$.^{14,15} The ratio $J(^{119}\text{Sn-C-H}) : J(^{117}\text{Sn-C-H})$ has been found to be 1.045.¹⁶ (In this thesis all correlations of tin-proton coupling constants have been made using $J(^{119}\text{Sn-C-H})$; therefore, for convenience, the symbol J will be used to denote this coupling constant.) Typical NMR data for a variety of dimethyltin compounds are listed in Table I. It is seen that J provides information concerning the structures of these compounds. For example, six-coordinate compounds with trans methyl groups have J values of about 100 Hz while five-coordinate compounds have values of about 77 Hz.

The factors influencing the magnitude of coupling constants are not well understood. In the Hamiltonian

describing the interaction of a proton directly bonded to a ^{13}C nucleus, the Fermi contact term was found to be dominant.^{24,25} Qualitatively, this term is a measure of the probability of the bonding pair of electrons existing at both nuclei. Since only s-orbitals have a finite probability at the nucleus, this term will be a measure of the percent s-character of the bond between the two nuclei. Fermi type coupling is also likely to be the principal contribution to coupling between protons in other molecules where there is no direct bond.²⁶

As a consequence of the Fermi contact term, information concerning the nature of the bonding in methyltin compounds can be obtained from J. A plot of percent s-character of the Sn-C bond vs. J for various methyltin compounds was shown to be linear,^{14,15} passing through the origin. Thus, knowledge of the coupling constant enables one to predict the mode of hybridization of the tin-carbon bonds. This treatment of J by Holmes and Kaesz¹⁴ assumes that $J(^{119}\text{Sn-C-H}) = 0$ for a pure $p\pi$ -orbital (the origin), that the nature of the C-H bonds do not change appreciably, and that the Fermi contact interaction dominates. Support for this interpretation is obtained from a recent study of trimethyltin chloride with various Lewis bases.²⁷ The changes in J could be explained

Table I

Nuclear Magnetic Resonance Data of Some Methyltin Compounds^{a,b}

Compound	$J(^{119}\text{Sn-C-H})$ (hz)	$\tau(\text{Sn-CH}_3)$ (ppm)	Coordination of Sn	Reference
$\text{R}_2\text{SnCl}_2^c$	69.7	8.85	4	14
$\text{R}_2\text{Sn}(\text{Ox})_2^d$	71.2	9.56	6(cis)	19
$\text{R}_2\text{SnCl}(\text{OAc})^e$	76.5	8.88	5	18
$\text{R}_2\text{Sn}(\text{pic})_2^f$	77.6	9.40	6	17
$\text{R}_2\text{SnCl}(\text{Ox})^d$	79.9	8.96	5	19
$\text{R}_2\text{Sn}(\text{OAc})_2^{c,e}$	82.5	9.09	6	20
$\text{R}_2\text{Sn}(\text{acac})_2^g$	99.3	9.51	6(trans)	17
$\text{R}_2\text{Sn}(\text{ClO}_4)_2^h$	107.0	-	-	17
$\text{RClSn}(\text{acac})_2^i$	120.9	9.09	6	21
$\text{R}_2\text{Sn}(\text{dtc})_2^{i,j}$	84.0	8.49	6	22
$\text{R}_2\text{SnCl}(\text{dtc})^i$	74.0	8.73	5	22
$\text{RClSn}(\text{dtc})^i$	108.0	8.48	6	22
$\text{R}_2\text{Sn}(\text{Trop})_2^{k,l}$	72.2	9.52	6	23
$\text{R}_2\text{SnCl}(\text{Trop})^l$	78.0	8.99	5	23

^a In CDCl_3 except where noted. ^b $\text{R} = \text{CH}_3$. ^c In CCl_4 .

^d Ox = 8-hydroxyquinolinato. ^e OAc = CH_3COO . ^f pic = picolinato.

^g acac = acetylacetonato. ^h In H_2O . ⁱ In CHCl_3 .

^j dtc = R_2NCSS . ^k Trop = tropolone. ^l In $\text{CHCl}_2\text{CHCl}_2$.

in terms of a model based on changes in s-character in the Sn-C bonds.

The relationship between percent s-character and J has been found to be not universally applicable. In studying dimethyltin bis (8-hydroxyquinolate) Kitching²⁸ suggested that extensive d-orbital participation is involved. The resulting hybridization, d^2sp^3 , would have about 17% s-character. However, with a J value of 71-72 Hz the relationship predicts 33% s-character.²⁸ Similarly, in a NMR study²⁹ of the pyridine adducts of $(CH_3)_3SnX$ and $(CH_3)_2SnX_2$, (X = Cl, Br, I) it was postulated that J is only proportional to the percent s-character for sp^n and not for sp^3d^n hybrid configurations. The increase in orbital overlap in the latter case was attributed to being parallel to the increase in orbital bond strength. The order of increase of J with bond strengthening was proposed to be: $sp^3d^2 > sp^3d > sp^3 < sp^2 < sp$. Finally, a heteronuclear double resonance NMR study of a series of methyltin halides¹⁶ has found an approximately linear correlation between $J(^{119}Sn-^{13}C)$ and $J(^{119}Sn-C-H)$. The line, however, does not pass through the origin, seriously questioning the assumption that $J(^{119}Sn-C-H) = 0$, for a pure $p\pi$ -orbital. This suggests that at least one of the coupling constants may involve significant contributions

from the electron orbital or dipole-dipole terms of the Hamiltonian.^{16,26}

2) Mössbauer Spectroscopy

The Mössbauer effect³⁰ is the recoilless emission and resonant reabsorption of those γ -rays which arise from nuclear excited states having lifetimes in the range 10^{-6} - 10^{-10} sec.³¹ Since the width of the γ -ray line is only about 10^{-12} of its energy, the energy can be modulated by moving the source of γ -rays relative to the absorber by 10^{-12} of the speed of light, about 1 mm/sec. A Mössbauer spectrum, therefore, consists of a plot of γ -ray counts vs. relative velocity of source towards absorber. Information of chemical interest^{32,33} are the bonding in compounds, obtainable from the isomer shift (IS) and their structure, obtainable from the quadrupole splitting (QS).

The Mössbauer effect for tin is generally studied by using the 245 - day isomer ^{119m}Sn as the parent nuclide.³⁴ This can be produced by a neutron irradiation of ^{118}Sn in a high flux reactor. The 89-keV metastable level of ^{119m}Sn decays by an isomeric transition directly to the 23.8-keV first excited state of ^{119}Sn . This Mössbauer level, with a spin of $+3/2$ and a half-life of 1.85×10^{-8} sec, then decays

by an M1 transition to the stable ground state with spin + $\frac{1}{2}$.

The expression for the isomer shift δ , for ^{119}Sn is given³⁵ by Equation 3,

$$\delta = 1.55 \times 10^{-29} (\delta R/R) [\psi_A^2(0) - \psi_s^2(0)] \text{ ev} \quad (3)$$

where $\delta R/R$ is the fractional change in the nuclear charge radius between the ground and the excited states; $\psi_s^2(0)$ and $\psi_A^2(0)$ are the total electron charge densities at the source and absorber nuclei, respectively. Since $\delta R/R$ is positive,³⁶ a positive isomer shift corresponds to an increase in s-electron density at the absorber nucleus compared with the source nucleus. While a single suitable standard has been found for the isomer shift of iron compounds³⁷ no such widespread standard exists for tin compounds. A number of different host matrices for the emitter nuclide have been successfully employed including metallic tin,³⁸ stannic oxide,³⁸ magnesium stannide,³⁸ and palladium tin alloys.³⁸ At the present time, the best source for ^{119}Sn spectroscopy appears to be barium stannate, BaSnO_3 .^{38,39} The relative isomer shifts between the different sources are known,^{38,39} enabling easy conversion between the various reports of organotin Mössbauer parameters.

Thus, it is seen that both the Mössbauer isomer shift

and the NMR coupling constant J are related to the electron density at the nucleus. It is not surprising that a linear relationship between isomer shift and J was found to exist for a series of methylstannanes⁴⁰ and methyltin chlorides.⁴¹ However, NMR spectra are run in solution while Mössbauer data are run as solids. Therefore, such a relationship may not be universally valid. The solution chemistry of organotin compounds will, in all likelihood, be more effectively studied through use of Mössbauer studies in frozen solutions.^{3,42,43}

For the frequently met case like tin, where the excited state has a total nuclear spin of $I = 3/2$, the expression for the quadrupole splitting, ΔE , is given⁴⁴ by Equation 4,

$$\Delta E = e^2 q Q/2 \quad (4)$$

where eq is the electric field gradient at the nuclear site, and eQ is the nuclear quadrupole moment. Although similar information (e.g., site symmetries, field gradients, and details of p- and d- electron imbalance) may be obtained from nuclear quadrupole resonance spectroscopy (NQR), Mössbauer spectroscopy has three important advantages over NQR³¹: (i) it is easier to measure; (ii) it is applicable to a wider range of nuclei; (iii) it is possible to get the sign as well as the magnitude of the field gradient.

The mere existence of the Mössbauer effect at room temperature (large recoil-free fraction) was taken⁴⁵ as an indication of a polymeric lattice structure. The ratio of quadrupole splitting to isomer shift (with respect to SnO_2) has been used⁴⁶ as criteria for tetrahedral (sp^3 hybridized) and non-tetrahedral (sp^3d hybridized or highly distorted tetrahedral) symmetry. The absence of a quadrupole splitting in a variety of asymmetric tetra- and hexacoordinate organotin compounds⁴⁶⁻⁴⁸ has been used as criterion for bonding. It was suggested⁴⁸ that electric field gradients and quadrupole interactions in such compounds are only observed when there is an imbalance in the presence of subsidiary π -interactions. The lack of a quadrupole splitting in compounds of the type $\text{R}_n\text{SnH}_{4-n}$ and $(\text{CH}_3)_3\text{SnNa}$ has been attributed to small changes in the state of hybridization at the tin atom and to back donation of electron pairs into the vacant 5d orbitals of tin.⁴⁹ However, it is now believed^{27,50} that electronegativity effects predominate.

Table II lists the Mössbauer parameters for various methyl- and phenyltin chelates. Inspection of this Table points up a structural correlation germane to the present study. The first three compounds, with a quadrupole splitting near 2mm/sec., are known by other physical measurements^{51,52}

TABLE II

Mössbauer Parameters for some Organotin Compounds^{a,b}

Absorber	Quadrupole Splitting (mm/sec.)	Isomer Shift ^c (mm/sec.)
$(C_6H_5)_2 Sn(acac)_2^{d,e}$	2.14	0.74
$(CH_3)_2 Sn(Ox)_2^f$	1.98	0.77
$(C_6H_5)_2 Sn(Ox)_2$	1.78	0.83
$(CH_3)_2 Sn(acac)_2$	3.93	1.18
$(CH_3)_2 Sn(imdp)_2^{g,h}$	4.18	1.28
$(CH_3)_2 Sn(pic)_2^i$	4.43	1.28
$(CH_3)_2 SnCl_2(phenan)^j$	4.03	1.32
$[(CH_3)_2 Sn(OAC)]_2 O^k$	3.57	1.38
$(CH_3)_2 Sn(OBz)_2^l$	3.96	1.40
$(CH_3)_2 Sn(OOCH)_2$	4.72	1.45
$(CH_3)_2 SnCl_2$	3.41	1.53
$(CH_3)_2 SnCl_2(bipy)^m$	4.09	1.55

^aAbsorber temperatures at about 80°K. ^bData from Ref. 53 except where noted. ^cWith respect to SnO₂. ^dacac = acetylacetonate.
^eRef. 51. ^fOx = 8-hydroxyquinolinato. ^gimdp = imidodiphosphate. ^hRef. 41. ⁱpic = picolinato.
^jphenan = 1, 10-phenanthroline. ^kOAC = CH₃COO. ^lOBz = C₆H₅COO.
^mbipy = 2,2'-bipyridyl.

to have cis methyl or phenyl groups. On the other hand, those compounds with a quadruple splitting near 4 mm/sec. have, in many instances, been assigned trans configurations. Therefore, it was proposed^{51,52} that $\Delta E_{\text{trans}} = 2\Delta E_{\text{cis}}$ for cis and trans R_2SnX_4 , (X = Cl, O, or N).

3) Infrared Spectroscopy

The movement of atoms and chemical bonds can be likened to that of a system comprised of springs and balls in constant motion,^{54,55} with stretching and bending vibrations. Perturbation of these systems with mechanical or electromagnetic (for molecules) energy increases their motion or amplitude of vibration. A significant difference between the two systems is that the vibrational energy levels of molecules are quantized; that is, the amplitude of the particular vibration is increased suddenly by a certain amount and not gradually.⁵⁴ Vibrations are excited by the absorption of light quanta of proper frequency (energy). The frequencies required occur in the infrared region of the spectrum. The absorption of energy from a beam of infrared radiation constitutes an absorption band. However, a vibration is not necessarily accompanied by an infrared absorption band. Absorption occurs only when the vibration causes a change in the dipole moment of the molecule. A

complement to infrared spectroscopy is Raman scattering, which occurs only when there is a change in polarizability of the molecule.^{54,56,57}

The infrared (IR) spectrum is said to be one of the most characteristic properties of a compound.⁵⁴ The great utility of IR spectroscopy originates from characteristic frequencies, absorption bands that appear with a relatively high intensity corresponding to a certain group of atoms such as the CH_3 group.⁵⁴ The position of these and other infrared bands often depend upon the state of the sample. For example, differences have been found between the spectrum of a solid measured as a Nujol mull and as a potassium bromide disc.⁵⁸ Also, shifts in band positions and intensities between gaseous, solid, and solution spectra may be caused by structural rearrangements. Infrared spectra of most organometallic compounds are run between $5000\text{--}300\text{ cm}^{-1}$.

Characterization of dimethyltin compounds by infrared spectroscopy is facilitated by the direct relationship that exists between the configuration of the dimethyltin moiety and the number of Sn-C bands in the $600\text{--}500\text{ cm}^{-1}$ region of the infrared spectrum. Group Theory⁵⁷ predicts that for the dimethyltin bis (chelates) a trans structure ($\text{C-Sn-C angle} = 180^\circ$) would have only one infrared active

band, assigned as the asymmetric Sn-C stretching vibration. A cis structure (C-Sn-C angle = 90°) would have two infrared active bands, including both asymmetric and symmetric Sn-C stretching vibrations. These two bands are usually found to have a range of 540-570 (asymmetric) and 509-530 (symmetric) cm^{-1} .⁵⁹⁻⁶¹

Such a marked difference between cis and trans configurations has proven to be useful as an indication of the mode of bonding. The assignments of a trans or cis configuration to a variety of dimethyltin chelates, listed in Table III, were based on the number and intensity of absorption bands appearing in the Sn-C region of the spectrum. The term non-linear is used to describe compounds which show a weak symmetric Sn-C stretching vibration--corresponding to a C-Sn-C configuration in between pure trans and pure cis. However, the chelate ligands may also have absorption bands in the tin-carbon region; therefore the interpretation of the spectra are not always simple.

Additional structural information concerning organotin carboxylates may be obtained from the COO stretching region, 1900-1300 cm^{-1} .⁶² The positions of the asymmetric and symmetric COO stretching frequencies have been used to indicate the presence of either a "free ester" carbonyl (Figure 1-b)

TABLE III

Sn-C Stretching Frequencies for some
Dimethyltin Chelates^a (cm-1)

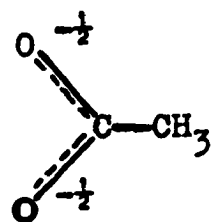
Chelate	Asymmetric	Symmetric	Configuration	Reference
$R_2Sn(acac)_2$ ^b	570 567 ^c	- -	trans	17
$R_2Sn(Ox)_2$ ^b	526	512	cis	19
$R_2Sn(Trop)_2$	529	513	non-linear	23
$R_2Sn(OAc)_2$	571	526	non-linear	20
$R_2Sn(dtc)_2$	559	513	non-linear	22
$R_2SnCl(Ox)$	567	514	cis	19
$R_2SnCl(Trop)$	569	521	non-linear	23
$R_2SnCl(OAc)$	578	528	non-linear	18
$R_2SnCl(dtc)$	555	515	cis	22

^aInfrared data except where noted; R = CH₃. ^bSee Tables I and II for meaning of symbols. ^cRaman.

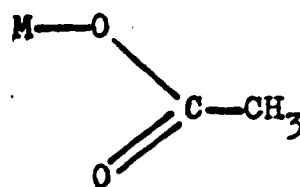
or a bridging carboxyl (Figure 1-d). For example, the asymmetric and symmetric COO vibrations for a series of trialkyltin carboxylates were found⁷ at about 1570 and 1410 cm^{-1} , respectively in the solid state. These bands, in dilute solution, shift to 1650 and 1300 cm^{-1} , respectively. X-ray^{2,63} and molecular weight studies⁶⁴ of some of these compounds have confirmed the presence of bridging carboxyl groups in the solid state as well as in very concentrated solutions.

The degree of separation, Δ , between the asymmetric and symmetric COO stretching vibrations provides additional structural information.^{65,66} Nakamoto⁶⁷ has suggested, however, that the use of Δ would not help in differentiating between internally chelating (Figure 1-c) or bridging (Figure 1-d) carboxylates. Both COO bands would be expected to shift in the same direction since the bond order of both bonds would be effected in the same manner. In fact, many authors⁶⁸⁻⁷¹ are of the opinion that no theoretical basis exists for distinguishing between the infrared spectra of ionic (Figure 1-a), internally chelating (Figure 1-c), and bridging (Figure 1-d) carboxylates.

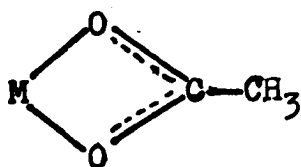
In surveying the infrared spectra for a large number of transition-metal acetates Edwards and Hayward⁷² found that the degree of separation of the COO stretching frequencies, Δ , could not be correlated with their known⁷² structural



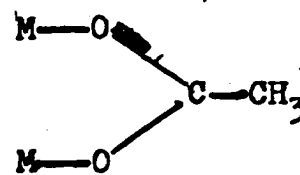
(a)



(b)



(c)



(d)

Figure 1. Modes of coordination for the acetate group. Taken from reference 67.

parameters. Table IV lists the infrared data of Edwards and Hayward along with the number of d-electrons for each transition metal. Two apparently different types of metal acetates are evident. Metal acetates with unfilled metal d-orbitals show a large range of Δ , while those with a d^{10} configuration have a value of Δ close to 140 cm^{-1} . In this paper it is suggested that the criticism of Edwards and Hayward only applies to metal acetates with unfilled metal d-orbitals. Metal-metal bonds and pi-bonding via the empty d-orbitals of the metal, known or proposed for many transition metal acetates,⁷²⁻⁷⁴ could conceivably effect the COO stretching vibrations. It would therefore, seem profitable to investigate the structural correlations of Δ for metal carboxylates with filled metal d-orbitals.

A third infrared band used to characterize organotin carboxylates is the tin-oxygen stretching vibration. Table V lists the range found for various Tin (IV) compounds. In view of the large shift of band position on changing compounds, most of the Sn-O assignments in the literature must be considered no better than tentative.

TABLE IV

COO Infrared Stretching Frequencies (cm⁻¹)^a

Acetate	Asym.	Sym.	Δ	No. d-electrons
V(III) ^b	1612	1431	181	2
Cr(II) ^c	1571	1422	149	4
Mo(II)	1585	1415	170	4
Mn(II)	1585	1410	175	5
Mn(II).4H ₂ O	1570	1400	170	5
Co(II)	1590	1405	185	7
Co(II).4H ₂ O	1550	1395	155	7
Rh(II) ^c	1588	1433	155	7
Ni(II)	1600	1415	185	8
Ni(II).4H ₂ O	1550	1425	125	8
Cu(II)	1595	1420	175	9
Cu(II).H ₂ O	1610	1410	200	9
Zn(II)	1550	1410	140	10
Zn(II).2H ₂ O	1550	1405	145	10
La(III)	1540	1410	130	10
La(III).1.5H ₂ O	1560	1420	140	10
Ce(III)	1550	1410	140	d
Ce(III).1.5H ₂ O	1565	1415	150	d
Ag(I)	1520	1405	115	10

^aAll data from Ref. 72 except where noted.

^bRef. 73.

^cRef. 75.

^d_{4d}¹⁰_{4f}

TABLE V

Sn-O Stretching Frequencies in Various Tin (IV) Compounds

Compound	Frequency Range (cm ⁻¹)	References
(R ₃ Sn) ₂ O	780-740	77
R ₂ Sn(OR') ₂	680-600 620-530	78
XYSn(Ox) ₂ ^{a, b}	540-510	19, 79
XYSn(acac) ₂ ^c	460-400	80
R ₃ SnOOCR'	410-280	64, 81
R ₂ Sn(OAc) ₂	305-280	20
[(OAc)R ₂ Sn] ₂ O ^d	652-610	21
Pyridine N-oxide complexes of tin	390-310	76

^aX and Y = alkyl, aryl, and/or halogen.

^bOx = 8-hydroxyquinoline.

^cacac = acetylacetonate.

^dOAc = CH₃COO.

4) Summary of Reported Configurations

Table VI summarizes the configurations of the dimethyltin moiety in dimethyltin bis (chelates) and dimethyltin chloride chelates as deduced by the NMR, Mössbauer, and IR spectra of these compounds. The term, non-linear, is used by many authors to denote a configuration where the C-Sn-C angle is somewhere in between 90° (pure cis) and 180° (pure trans). Inspection of Table VI shows that in most cases, the predictions of these physical methods are in agreement with each other. Dimethyltin bis (picolinate) appears to be the only exception. NMR spectra ($J = 77.6 \text{ Hz}$)¹⁷ predicts a non-linear configuration, while Mössbauer effect studies ($\Delta E = 4.43 \text{ mm/sec.}$)⁵³ predicts trans methyl groups. However, this may be caused by a change in structure in going from the solid to solution.

B. Exchange Studies

In organotin chemistry the redistribution reaction between a tetraalkyl - or tetraaryltin and tin tetrahalide, originally developed by Kocheshkov,⁸² plays an important role in the preparation of organotin halides.¹ Although the synthetic utility of this reaction has been thoroughly investigated,⁸³ there have been few quantitative studies of

TABLE VI

Summary of Configurations for Some Dimethyltin Chelates

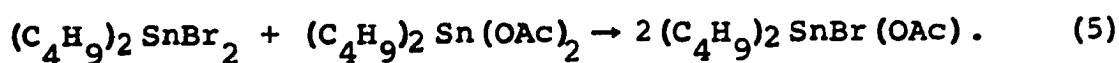
Chelate ^a	NMR	Mössbauer	IR
$R_2Sn(acac)_2$	trans	trans	trans
$R_2Sn(Ox)_2$	cis	cis	cis
$R_2Sn(pic)_2$	non-linear	trans	-
$R_2Sn(OAc)_2$	non-linear	-	non-linear
$R_2Sn(Trop)_2$	non-linear	-	non-linear
$R_2Sn(dtc)_2$	non-linear	-	non-linear
$R_2SnCl(Ox)$	non-linear	-	cis
$R_2SnCl(OAc)$	non-linear	-	non-linear
$R_2SnCl(Trop)$	non-linear	-	non-linear
$R_2SnCl(dtc)$	cis	-	cis

^a $R = CH_3$

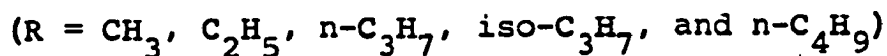
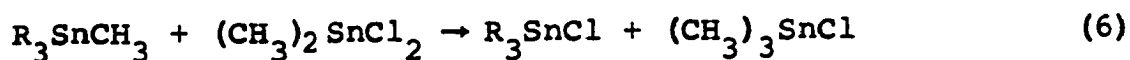
See Tables I, II, and III for meaning of symbols.

reactions involving the scrambling of substituents on tin.^{84,84a.}

Redistribution reactions involving the dimethyltin moiety have only recently been recognized and investigated. Alleston and Davies⁸⁵ have prepared dibutyltin bromide acetate according to Equation 5,



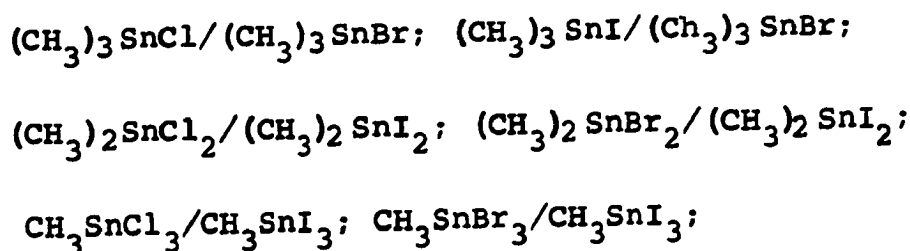
The rate of interchange of halogen atoms for sulfur bridges in mixtures of dimethyltin dihalide and trimeric dimethyltin sulfide was found⁸⁶ to be fastest when the halogen atom is chlorine and slowest for iodine. A kinetic study of reactions of the following type:



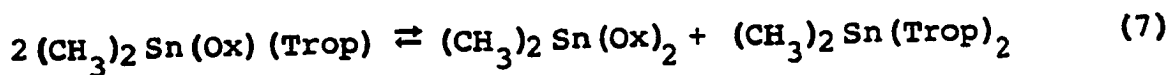
shows that these reactions take place only in those media which allow dissociation of the dimethyltin dichloride.⁸⁷

Nuclear magnetic resonance spectroscopy has been found to be very useful in studying rapid exchange reactions in an equilibrium system. The existence of more than one Sn-CH_3

peak was found in the NMR spectra of the following mixtures:⁸⁸



indicating a slow rate of halogen exchange. The rate of halogen exchange between these methyltin halides was found to decrease with increasing number of halogen substituents. In an analogous study, the NMR spectrum of a mixture of dimethyltin bis (8-hydroxyquinolate) and dimethyltin bis (tropolonate) showed three methyl proton signals at 20°C.⁸⁹ Two of these signals were assigned to starting materials while the third was assigned to the mixed chelate, dimethyltin (8-hydroxyquinolate) (tropolonate). A single methyl proton signal was observed at 87°C. This supports the following equilibrium:



(Ox = 8-hydroxyquinolate; Trop = tropolonate).

In a related reaction, an equimolar solution of dimethyltin dichloride and dimethyltin bis (tropolonate)

showed only one methyl proton signal at room temperature.²³ However, heating above 100°C produced two additional methyl proton signals. It was suggested that above 100°C the predominant reaction is



where X = Cl, Br, or I. This pronounced lability of ligands coordinated to methyltin compounds is consistent with the fact that coordinated methyl groups are very effective in reducing the charge and in labilizing the other ligands in the first coordination sphere of metal ions.^{90,91}

CHAPTER II

THEORETICAL BACKGROUND

A. Trends in Group IV Organometallic Chemistry.

The differences in chemical behavior and structure of organometallic compounds of Si, Ge, Sn, and Pb have their origin in the electronegativity differences, the increasing atomic radius in going from carbon to lead, and in the ability of elements other than carbon to expand their coordination number by using their d-orbitals. Table VII lists the properties of bonds between carbon and the Group IV elements.

Different authors have assigned different electronegativity values to the Group IV elements. For example, Pauling⁹⁵ and others⁹⁶ conclude that the electronegativity decreases in going from carbon to lead. Sanderson^{97,98} and Allred and Rochow,^{99,100} on the other hand, proposed alternating electronegativity values. The values assigned by some authors are compiled in Table VIII. Since the differences in electronegativities are not very pronounced, electronegativities are of a limited value in understanding differences in reactivity of Group IV organometallic compounds.

TABLE VII

Distances and Bond Strengths Between
Carbon and Group IV Elements

Element	Covalent Radius ^a (Å)	M-C Distance ^b (Å)	M-C Bond Strengths ^c (KCal)
C	0.77	1.54	83
Si	1.13	1.90	60
Ge	1.21	1.98	-
Sn	1.41	2.18	54
Pb	1.52	2.29	31

^aReference 92.

^bReference 93; in tetraalkyl compounds.

^cReference 94.

TABLE VIII

Electronegativity Values Assigned by Various Authors

<u>Element</u>	<u>Pauling^a</u>	<u>Pritchard and Skinner^b</u>	<u>Allred and Rochow^c</u>
C	2.5	2.5 - 2.6	2.55
Si	1.8	1.8 - 1.8	1.90
Ge	1.7	1.8 - 1.9	2.01
Sn	1.7	1.8 - 1.9	1.96
Pb	-	1.8	2.33

^a Reference 95.

^b Reference 96.

^c References 99.

Inspection of Table VII shows that the covalent radius increases in the order $C < Si < Ge < Sn < Pb$. The results of this increase are: (a) decreased steric shielding with increased atomic radius; (b) diminished bond energy with increasing interatomic distances; (c) increased polarizability in the order Si, Ge, Sn, and Pb; (d) increased maximum covalence for elements following carbon through use of d-orbitals. The first three effects facilitate attack by polar reagents on the organometallic compounds of Group IV. The last effect is directly involved in the formation of coordination numbers greater than four and in the mechanisms involved in the reactions of organometallic compounds of Si, Ge, Sn, and Pb.

B. Geometry and Coordination Number of Tin.

While carbon has a maximum coordination number of four, tin is able to increase its coordination number to five,^{7,63} six,¹¹ seven,^{12,101} and even eight.^{102,103} This is possible since tin has low energy d-orbitals available for expanding its coordination number. Three theoretical approaches describing the geometry of organotin chelates with coordination numbers of five and six will now be discussed.

Valence-Bond theory^{104,105} explains five-coordinate tin compounds by $sp^3 d_z^2$ and $sp^3 d_{x^2-y^2}$ hybridization for trigonal-bipyramid and tetragonal-pyramid geometries, respectively. It has already been pointed out¹⁰⁶ that interconversion of the two idealized geometries requires only a bending process as shown in Figure 2. For an ML_5 species such a process is a genuine vibration; therefore, distinction between the two is not very meaningful.¹⁰⁷ In compounds such as $(CH_3)_2SnX(Chelate)$, the influence of the bidentate chelate on the C-Sn-C configuration (and therefore, on J) is not at all clear. The rigidity of the chelate could prevent the interconversion process, stabilizing either of the two geometries. The opposite effect is produced by the coordinated methyl groups labilizing the other ligands.^{90,91} Clearly, any structural considerations of five-coordinate species must refer to a particular physical state. X-ray studies of five-coordinate organotin carboxylates have only found trigonal-bipyramid geometries.⁶³ Consequently, only this geometry will be discussed, but a tetragonal-pyramid will be considered when discussing physical states other than the solid.

The Valence Shell Electron Pair Repulsion (VSEPR) model, originated by Gillespie,¹⁰⁸ predicts that the ligands

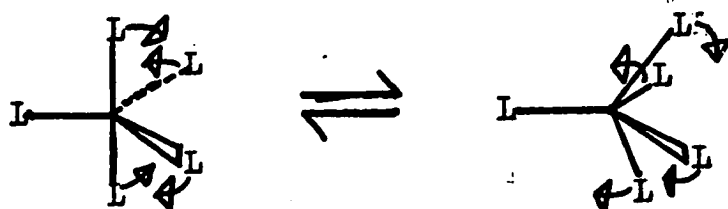


Figure 2. Interconversion of trigonal-bipyramid into tetragonal-pyramid.

of lesser electronegativity occupy the equatorial positions in trigonal-bipyramids. For compounds such as $R_2SnX(\text{carboxylate})$ this model prefers a non-linear C-Sn-C moiety (Figure 3-c).

In discussions of the bonding in organotin chelates it was postulated^{17,109} that the two Sn-C bonds would be essentially sp^2 hybrids (Figure 3-c) in the equatorial plane while the remaining p-orbital participates in an approximately linear three-center bond (one bonding pair of electrons for two bonds). This type of bonding has been proposed for the interhalogen compounds¹¹⁰ and for the xenon fluorides.¹¹¹ Thus, while the Valence-Bond approach makes no prediction concerning the geometry of the C-Sn-C moiety, both the other models agree that it is non-linear, specifically predicting Figure 3-c as the preferred configuration.

For six-coordinate tin the Valence-Bond theory predicts an octahedral arrangement by $sp^3 d_z^2 d_{x^2-y^2}^2$ hybridization. For such an octahedral structure involving dimethyltin the two bonds of the C-Sn-C skeleton have also been proposed to be constructed from essentially sp hybrids.¹⁷ The remaining two p-orbitals of tin can form two sets of three-center bonds in the plane approximately perpendicular to the C-Sn-C axis, corresponding to Figure 3-e. The VSEPR model predicted an undistorted octahedral configuration in compounds such as

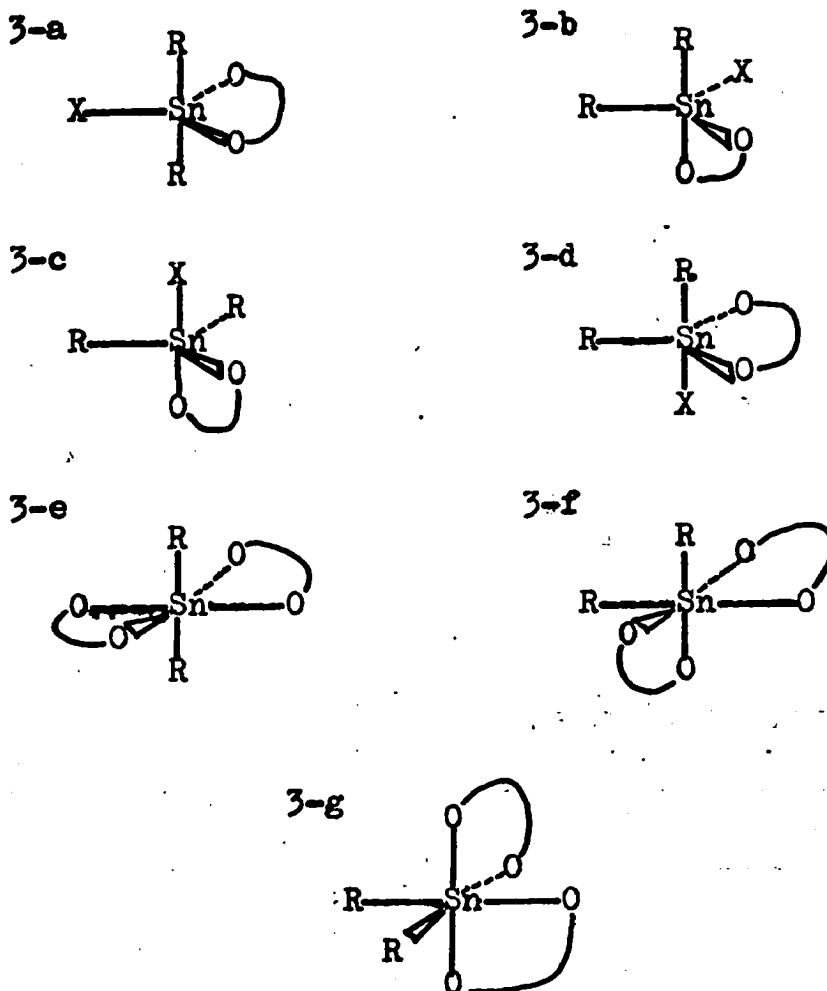


Figure 3. Possible configurations of $R_2SnX(\text{carboxylate})$ and $R_2Sn(\text{carboxylate})_2$.

SnCl_6^{2-} .¹⁰⁸ For $\text{R}_2\text{SnCl}_4^{2-}$ this model predicts that the electropositive alkyl groups would avoid each other, that a trans C-Sn-C moiety is preferred for dialkyltin bis (carboxylates). It should be noted, though, that there is evidence¹¹ for cis alkyl groups (corresponding to Figure 3-f) in the solid. There does not appear to be any simple explanation for this discrepancy.

C. Bonding.

1) The occurrence of (p → p) π double bonding

Double bonding involving p-orbitals from both the metal and the ligand has not been found for either Si, Ge, Sn, or Pb.¹¹² The non-existence of such double bonding was attributed by Beattie and Gilson¹¹³ to the fact that the alternative possibility, involving the use of d-orbitals, is energetically more favorable.

2) Use of d-orbitals

In addition to the normal sigma-bond three types of bonding involving d-orbitals are possible. These are acceptive $d\sigma$ -bonding, acceptive π - bonding, and dative π -bonding.

Acceptive $d\sigma$ -bonds result when a ligand donates a pair of electrons with σ -symmetry into empty low energy d-orbitals of any of the Group IV elements, except carbon. This results

in an increased coordination number for the metal. For example, reaction of $(\text{CH}_3)_3\text{SnCl}$ with pyridine forms a five-coordinate 1:1 addition compound.¹⁰⁹

Acceptive π - bonding is of two types; ($p \rightarrow d$) π - bonding results either by overlap of the π - orbitals of a ligand having a free electron pair or by overlap of the π - electron system of olefinic, acetylenic, or aromatic groups with suitable low energy d-orbitals of the metal. The resulting metal-ligand bond acquires double-bond character. The properties of Si, Ge, Sn, and Pb bonded to groups such as phenyl,^{114,115} oxygen, nitrogen, and halogen,¹¹⁶ have been explained in terms of such ($p \rightarrow d$) π - bonding.

The effect of ($p \rightarrow d$) π - bonding in $(\text{alkyl})_3\text{MOC}_6\text{H}_5$, ($M = \text{Si, Sn, or Pb}$) is to remove electron density from the oxygen into the empty d-orbitals of the central atom. In going from silicon to lead the principal quantum number of these d-orbitals increases. Therefore, no extensive π - bonding of this type is expected between tin and oxygen, because of decreased overlap and poorer matching of the orbitals.¹¹⁷ Similar conclusions have been made for other compounds where tin is bonded to oxygen,¹¹⁸ sulfur,¹¹⁸ and nitrogen.¹¹⁹

Dative π - bonding results from donation of electrons from filled metal d-orbitals into suitable (e.g., antibonding) orbitals of the ligands. Such ($d \rightarrow p$) π - bonding is synergic with the acceptive d σ - bonding mentioned above.

A summary of the types and effects of bond formation involving the d-orbitals of the Group IV elements is given in Table IX. Acceptive d σ - bonding is seen to be most common with tin and lead, enabling these elements to expand their coordination numbers relative to Si and Ge. The greatest acceptive ($p \rightarrow d$) π - bonding is expected for silicon; but even here some experimental evidence^{111,117,119} does not seem to support such π - bonding.

Ahrland, Chatt, and Davies¹²⁰ and Pearson¹²¹ have classified Lewis acids into two major categories: "hard" or class (a) acids and "soft" or class (b) acids. According to Chatt^{122,123} the important features of class (b) acids is the presence of loosely held outer d-orbital electrons which can form π - bonds by donation to suitable ligands. The existence of dative ($d \rightarrow p$) π - bonding for tin and probably lead would make them "soft," class (b) metals with stabilized complexes with 2nd and 3rd row elements.¹²⁴ In short, while present evidence seems to indicate no extensive ($p \rightarrow d$) π - bonding for Si, Ge, Sn, or Pb, the increased soft,

TABLE IX

d-Orbitals and Bond Formation of Group IV B Elements^a

Element	Acceptive ^b d σ - bonding	Acceptive (p $\rightarrow$ d) π -bonding	Dative (d $\rightarrow$ p) π -bonding
C	-	-	-
Si	<u>+</u>	++ ^c	-
Ge	<u>+</u>	+ ^c	+ ? <u>-</u>
Sn	++	<u>+</u>	+
Pb	++	<u>+</u>	+

^aAdapted from reference 112, p. 91.

^bKey: - absent
 + weak or absent
 + present but not strong
 ++ strong

^cSee text.

class (b) character of the Group IV elements should parallel the increase in acceptive d σ - bonding and dative (d $\rightarrow$ p) π - bonding in the order Si < Ge < Sn < Pb.

3) Sn-O bond

It has been proposed¹⁷ that the nature of the tin-oxygen bond has a direct influence on the geometry of organotin chelates possessing such bonds. For compounds such as R_2Sn (acetylacetonate)₂, there are two relatively nonpolar tin-carbon bonds and four highly polar tin-oxygen bonds. As already noted, the C-Sn-C bonds have been described^{17,109} in terms of sp hybrids explaining the linearity of this group. However, as the bonds in the equatorial plane become more like the axial Sn-C bonds (i.e., more covalent), the tin 5s-character should become more uniformly distributed among all six bonds. This should result in a lowering of J and a non-linear C-Sn-C moiety.

This approach would classify six-coordinate diorganotin bis (chelates) into three types: (i) highly polar tin-oxygen bonds, a trans (linear) C-Sn-C skeleton, and high J values (90 Hz); (ii) covalent tin-oxygen bonds, cis organic groups, and low J values (73 Hz); (iii) tin-oxygen bonds with both ionic and covalent character, a C-Sn-C angle in between pure cis and pure trans, and intermediate J values (75-85 Hz).

While this classification seems to agree with other physical measurements (see Table VI), it assumes that the Fermi contract term dominates the spin-spin coupling, a point already seriously question.^{16,26}

Initial studies^{59,125} of organotin carboxylates indicated the presence of ionic tin-oxygen bonds. Subsequently, this data was interpreted^{7,68,126,127} in terms of bridging carboxyl groups. The nature of the tin-oxygen bond, is, therefore, expected to depend upon the mode of coordination of the carboxyl group. In going from solid to solution the mode of coordination of the carboxyl group changes from bridging (Figure 1-d) to "free-ester" (Figure 1-b) for trialkyltin carboxylates^{2,17,63} and from bridging to bidentate-internally chelating (Figure 1-c) for dialkyltin bis (carboxylates).²⁰

The order of the preferred mode of coordination of the carboxyl group in solution would then be:

"free-ester" > internal chelation > bridging.

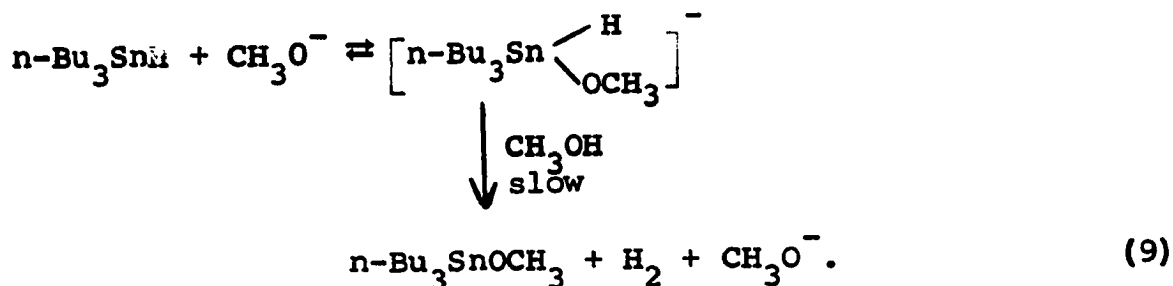
It is tempting to consider this order to parallel the tin-oxygen bond strength. However, this relationship does not correlate with other chelates. Triorganotin (8-hydroxy-quinolates) have been shown^{19,128} to contain internally

chelated structures in solution. Unfortunately, the Sn-O stretch in the infrared spectra of the various compounds overlap each other (see Table V), making accurate force-constant calculations impossible. Finally, the labilizing effect of the methyl groups^{90,91} apparently weakens the Sn-O bond. This may explain why triorganotin compounds prefer a "free-ester" while diorganotin compounds prefer internal chelation in solution.

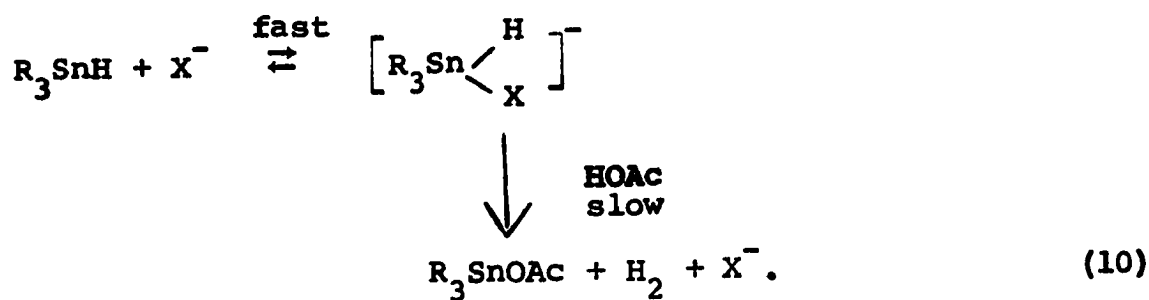
D. Exchange Reactions.

1) General

The isolation of five coordinate organotin compounds has been of considerable assistance in studying the reaction mechanisms of organotin compounds. This is because five-coordinate intermediates are believed to occur in a variety of exchange and redistribution reactions involving organotin compounds. For example, Kuivila and Levins¹²⁹ proposed that the base-catalyzed protonolysis of tributyltin hydride in basic methanol solution proceeds through the prior formation of a five-coordinate intermediate as shown by Equation 9,

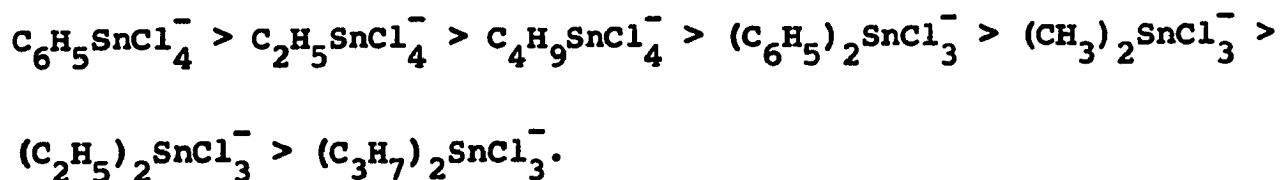


A similar type of intermediate was proposed by Dessy, Hieber, and Paulik¹³⁰ who found that the rate of acetolysis of tributyltin hydride in dimethyl-sulfoxide solution was markedly increased by halide ions as shown by Equation 10,



In studying various methyltin halogen systems, such as $(\text{CH}_3)_3\text{SnBr}/(\text{CH}_3)_3\text{SnCl}$, it was found that the rate of halogen exchange tends to be greater in CHCl_3 than in CCl_4 . This was taken⁸⁸ as an indication that exchange proceeds through an ionic intermediate which is probably five-coordinate, as $(\text{CH}_3)_3\text{SnBrCl}^-$. In an analogous approach, the reaction of $\text{R}_3\text{Sn-CH}_3$ with $(\text{CH}_3)_2\text{SnCl}_2$ to produce R_3SnCl was pictured⁸⁷ as proceeding through a five-coordinate, anionic species of the type $(\text{CH}_3)_2\text{SnCl}(\text{S})_2^+$ or $(\text{CH}_3)_2\text{Sn}(\text{S})_3^{+2}$ (S = coordinating solvent such as methanol).

It is worthwhile to consider the reasons why tin readily forms five-coordinate organotin compounds. The relative stabilities of organotin chloride anionic species were found¹³¹ to decrease in the following order:



This order of stabilities implies that organotin trichlorides, RSnCl_3 , form a more stable complex with chloride ion than the analogous diorganotin dichlorides, R_2SnCl_2 . This has been explained¹³² by the greater ability of RSnCl_3 to delocalize the charge built up on formation of the coordinate chlorine bond relative to R_2SnCl_2 . Simultaneously, the greater number of chlorine atoms in RSnCl_3 are better able to decrease the diffuse character of the d-orbitals of tin to make them more accessible to some sort of π - bonding.^{132,133}

In addition to the electronegativities of the groups attached to tin, the availability of d-orbitals certainly aids the tin atom to expand its coordination number to five (and even six). This was pointed out by Eaborn and Pande's^{130,134} study of the rate of cleavage of the phenyl group from $\text{R}_3\text{M}-\text{C}_6\text{H}_5$. The relative rates of cleavage were 1:36:3.5 $\times 10^5$:2 $\times 10^8$ for Si, Ge, Sn, and Pb, respectively; and a five-coordinate intermediate was proposed, which from the rates, seems particularly important for tin and lead.

From the point of view of the various types of d-orbital participation previously mentioned, it seems that dative

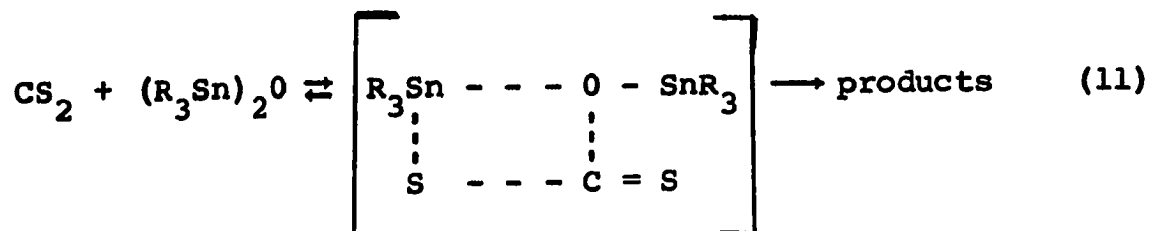
(d → p) π - bonding enables tin to expand its coordination number by a synergic effect on the σ-system. It is this type of bonding which also explains another implication of the order of stabilities listed above. Inspection shows that the phenyl compounds are always more stable than the analogous alkyl compounds. Although Zanella and Tagliavini¹³¹ attributed this to the difference in electronegativities between alkyl and aryl groups, the stability of the phenyl compounds could be explained by delocalization of negative charge into the phenyl ring by dative (d → p) π - bonding.

2) R_2SnX_2 and $R'_3SnOOCR''$.

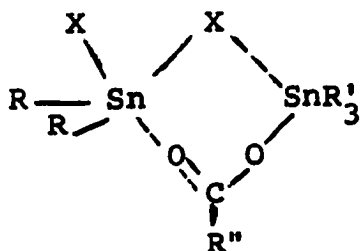
There are many possible mechanisms to describe the reaction of R_2SnX_2 and $R'_3SnOOCR''$ to form $R_2SnX(OOCR'')$ and R'_3SnX . One possibility is a dissociative mechanism on the order of an S_N1 or S_E1 mechanism. While R_2SnX_2 has been known to form solvated cations,⁸⁷ such a mechanism would require the $R''COO$ group to split off from R'_3Sn , forming R'_3Sn^+ and $R''COO^-$. But infrared spectra^{7,126,127} showed that the compound remains intact as $R'_3SnO - \overset{O}{\parallel}CR''$. An S_E2 mechanism can safely be discarded since there are no available electrophiles.

A four-center transition state was proposed by Reichle¹³⁵

to describe the reaction of CS_2 with $(\text{R}_3\text{Sn})_2\text{O}$ as in Equation 11,



In addition, there is evidence^{18,136} of halogen bridging in five-coordinate organotin compounds. It is, therefore, probable that reaction of R_2SnX_2 with $\text{R}'_3\text{SnOOCR''}$ involves an $\text{S}_{\text{N}}2$ mechanism, with an intermediate involving expansion of the coordination of both tin atoms to five:



Because of the existence of a free carbonyl in dilute solutions of triorganotin carboxylates it is probable that the reaction is initiated by attack of the oxygen lone-pair onto the other tin atom. The close proximity of the triorganotin species then enables the halogen to bridge the two tin atoms. Breaking of the $\text{R}'_3\text{Sn-O}$ and $\text{R}_2\text{XSn-X}$ bonds enables the products to then form.

The validity of the proposed mechanism may be tested in many ways. The requirement of a nucleophile means that triorganotin chelates with no readily available pair of electrons would be expected to have a much slower rate of chelate exchange with R_2SnX_2 than the analogous triorganotin carboxylates. Second, the rate should also, in some way, depend upon the ability of the halogen to form bridges (e.g., different halogens should have different rates). Third, electron withdrawing groups attached to any of the organic groups on either reactants should increase the rate. Conversely, electron donating groups should decrease the rate. Finally, chelates with second row elements as donors (e.g., triorganotin dithiocarboxylate) should enhance the rate since such atoms are better able to expand the coordination number of tin by dative ($d \rightarrow d$) π - bonding than chelates with first row elements as donors.

CHAPTER III

OUTLINE OF EXPERIMENTAL APPROACH

In this chapter the experimental procedures used in this investigation will be briefly outlined. The reasons for choosing these approaches are also indicated. This provides an overall view of the scope and direction of the present study. Detailed results are given in Chapter IV and discussion is reserved for Chapter V.

A. Dimethyltin bis(carboxylates).

To ascertain how subtle differences in the donor properties of a chelate might influence the nature of the bonding around the dimethyltin moiety, a series of dimethyltin bis(p-substituted benzoates) were prepared. The compounds were chosen such that the Hammett σ_p constants¹³⁷ of the parent acids varied over a range of -0.66 to +0.78. The σ_p and pK_a values are listed in Table X.

These compounds were synthesized using four different procedures: (a) the method of O'Hara, Okawara, and Nakamura¹³⁸ reacting dimethyltin dichloride with the ammonium salt of the acid in a homogeneous solution;

TABLE X

Hammett σ_p Constants and Acid Strengths

For $p\text{-XC}_6\text{H}_4\text{COOH}$

X	σ_p^a	pK_a^b
NO_2	+0.78	3.41
CN	+0.63	3.55
Cl	+0.23	4.03
H	0.00	4.17
CH_3	-0.17	4.36
CH_3O	-0.27	4.49
NH_2	-0.66	4.92

^aData from reference 137. ^bData from reference 141 and 142.

(b) the method of Razuvaev, Shchepetkova, and Vyazankin¹³⁹ reacting the tetramethyl 1,3-dibenzoate distannoxane with the acid; (c) the method of refluxing dimethyltin oxide with the acid; (d) the method of Frankel, Gertner, Wagner, and Zilkha¹⁴⁰ reacting dimethyltin dichloride with the sodium salt of the acid at an interface.

Except for dimethyltin bis(benzoate), the bis(benzoates) are new compounds. They were characterized by elemental analysis and molecular weights. The NMR and infrared spectra of these compounds were what would be expected for compounds of similar structures. The detailed properties of these compounds are listed in Tables of Chapter IV.

The influence of the para-substituent on the s-electron density of the tin atom was studied by examining both the NMR spectra of these compounds for any regular change in the tin-methyl coupling constant, $J(^{119}\text{Sn-C-H})$ and the Mössbauer spectra for any regular change in isomer shift, δ_0 , and quadrupole splitting, ΔE .

The polymeric nature of these compounds was investigated by looking for a Mössbauer effect at room temperature.⁴⁵ To test the Fitzsimmons relationship that $\Delta E_{\text{trans}} = 2\Delta E_{\text{cis}}$,^{51,52}

these compounds were also examined for a Mössbauer effect at 80°K, and compared with those structures predicted from NMR and infrared spectra.

In order to confidently assign the COO, Sn-C, and where possible, the Sn-O stretching vibrations, a more or less complete assignment of the infrared spectra of these compounds was made. This was facilitated by comparison with the corresponding sodium salts of the acids.

The linearity of the C-Sn-C moiety was determined by inspecting the 600-500 cm^{-1} region for one or two Sn-C stretching vibrations.⁵⁷ The existence of a bridging or bidentate carboxyl group was detected by noting the change of the positions of the asymmetric and symmetric COO stretching vibrations in going from the solid to solution. The usual infrared criteria for deciding between these two modes of the carboxyl group are not very clear-cut, as mentioned in Chapter I. It was found that comparing the separation of the asymmetric and symmetric COO stretching vibrations of the compounds in the solid and in solution with the analogous separation of the corresponding sodium carboxylates was more useful.

For comparison with aliphatic carboxylates with a markedly different acid strength, dimethyltin bis

(monochloroacetate) was also prepared. Data on other aliphatic carboxylates of dimethyltin was obtained from the literature. The aliphatic and aromatic carboxylates of dimethyltin were compared to determine the extent to which the acid strength of the carboxylate and the π - system of the benzene ring influence the structures and properties of these compounds.

B. Dimethyltin Halide Carboxylates.

The influence of subtle differences in donor properties of the carboxylates on the reactivity of the dimethyltin bis (benzoates) was investigated by reaction of these compounds with dimethyltin dichloride to form dimethyltin chloride benzoates. This approach, as well as three other methods of synthesis did not yield the desired product. However, dimethyltin chloride monochloroacetate was able to be synthesized using these methods. Diphenyltin chloride benzoate was prepared using a new synthetic approach (see below). The NMR, infrared, and Mössbauer spectra of these compounds were compared with similar data for the corresponding diorganotin bis (carboxylates) as well as with the data for dimethyltin chloride acetate.

C. Exchange Reactions.

In order to understand the apparent instability of the dimethyltin halide benzoates, the NMR spectra of solutions containing varying relative concentrations of dimethyltin dichloride and dimethyltin bis (p-methoxybenzoate) were compared. A single tin-methyl peak was found at all concentrations and temperatures. Solutions of dimethyltin dichloride and trimethyltin benzoate, with significantly different τ (Sn-CH_3) values, were also studied by NMR spectra. The J values of the dimethyltin species indicated the presence, in solution, of five- and six-coordinate tin for a 1:1 and a 1:2 mole ratio, respectively. These results were confirmed by isolating dimethyltin bis (benzoate) from a solution containing dimethyltin dichloride and trimethyltin benzoate in a 1:2 mole ratio, respectively. This reaction was extended to systems such as dimethyltin dichloride with the following triorganotin carboxylates: $(\text{CH}_3)_3\text{Sn}(\text{OOCCH}_2\text{Cl})$, $(n\text{-C}_4\text{H}_9)_3\text{Sn}(\text{OOC}_6\text{H}_5)$, $(\text{C}_6\text{H}_5)_3\text{Sn}(\text{OOCCH}_3)$, and $(\text{C}_6\text{H}_5)_3\text{Sn}(\text{OOC}_6\text{H}_5)$ as well as to diphenyltin dichloride with $(\text{CH}_3)_3\text{Sn}(\text{OOC}_6\text{H}_5)$. Depending upon the system and the mole ratio, simple crystallization yielded the following: $(\text{CH}_3)_2\text{Sn}(\text{OOC}_6\text{H}_5)_2$, $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_3)$, $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$, $(\text{CH}_3)_2\text{Sn}(\text{OOCCH}_2\text{Cl})_2$, $(\text{C}_6\text{H}_5)_2\text{SnCl}(\text{OOC}_6\text{H}_5)$, and $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{OOC}_6\text{H}_5)_2$.

The mechanism of these reactions as well as the stability of five-coordinate organotin carboxylates were tested by studying the reactions of diorganotin chloride carboxylates with triorganotin carboxylates in a 1:1 mole ratio.

CHAPTER IV

PRESENTATION OF RESULTS

A. Introduction.

In this chapter the data obtained in this investigation are presented without detailed discussion because the conclusions depend upon the several different sets of data together rather than separately. Full discussion is reserved for Chapter V.

B. New Compounds.

All new compounds synthesized in this work are listed in Table XI. Detailed descriptions of the methods of synthesis are given in Chapter VII.

C. Dimethyltin bis (benzoates).

The dimethyltin bis (benzoates) were characterized by their melting points and analysis as shown in Table XII along with similar data for other diorganotin bis (chelates) synthesized. Molecular weight data for the soluble dimethyltin bis (benzoates) are listed in Table XIII. The NMR spectra of the dimethyltin bis (benzoates) and dimethyltin bis (monochloroacetate) are shown in Figures 4-10. Except where indicated all samples were analyzed at about 40°C in

CDCl_3 using TMS as internal standard. The relevant portions of these spectra are tabulated in Table XIV.

The Mossbauer parameters for the dimethyltin bis (carboxylates) at 77°K are shown in Table XV. Detailed spectra are shown in Appendixes 1-9. Mossbauer data at room temperature are listed in Appendix 11-a.

The infrared spectra of all diorganotin bis (carboxylates) are shown in Figures 11-26. Samples were run in KBr discs, nujol mulls, and, where soluble, in chloroform solution. A complete tabulation of all spectra is given in Appendixes 12-22. Tables XVI-XIX list the Sn-C, COO, and Sn-O stretching frequencies for the diorganotin bis (carboxylates) as well as the COO stretching frequencies for the sodium carboxylates.

D. Exchange Reactions.

The results of NMR studies of mixtures of various organotin chlorides and organotin benzoates are listed in Table XX. The variation of J for the dimethyltin species with increasing concentration of $(\text{p-CH}_3\text{OC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$, $(\text{CH}_3)_3\text{Sn}(\text{OOCCH}_2\text{Cl})$, and $(\text{CH}_3)_3\text{Sn}(\text{OOCCH}_2\text{Cl})$ are shown in Figures 27-29, respectively. Table XXI shows the results of those reactions where chemical separation of the products were attempted.

E. Diorganotin Halide Carboxylates.

Attempts to isolate dimethyltin halide benzoates are summarized in Table XXII. The melting points and analysis of the two diorganotin chloride carboxylates synthesized appear in Table XXIII. Figures 30 and 31 show the NMR spectra of $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$ and an equimolar solution of $(\text{CH}_3)_2\text{SnCl}_2$ and $(\text{p-CH}_3\text{OC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ respectively. Mössbauer spectra of dimethyltin chloride carboxylates are shown in Appendixes 10 and 11. Tables XXIV and XXV list the NMR data and the Mössbauer data, respectively, for these compounds. Relevant infrared data for new and representative diorganotin halide carboxylates are listed in Tables XXVI XXVIII.

TABLE XI

NEW COMPOUNDS

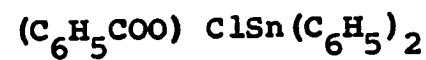
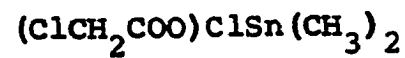
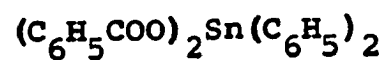


TABLE XII

Melting Points and Analysis of $(CH_3)_2Sn(OOCR)_2$

R	m.p. ($^{\circ}C$)	%Sn Found (Calcd.)	%C Found (Calcd.)	%H Found (Calcd.)	%Cl Found (Calcd.)	%N Found (Calcd.)
C_6H_5	161.5-163	30.15 (30.35)	48.95 (49.14)	4.21 (4.13)	-	-
$p\text{-}ClC_6H_4$	201.5-203	25.70 (25.81)	41.56 (41.78)	3.11 (3.08)	15.48 (15.42)	-
$p\text{-}NH_2C_6H_4$	226-228	27.99 (28.19)	45.94 (45.64)	4.46 (4.32)	-	6.40 (6.66)
$p\text{-}NO_2C_6H_4$	281-282	24.62 (24.68)	40.03 (39.95)	2.98 (2.92)	-	5.57 (5.83)
$p\text{-}CH_3OC_6H_4$	171-173	26.26 (26.31)	48.07 (47.93)	4.73 (4.48)	-	-
$p\text{-}CH_3C_6H_4$	126-129	28.73 (28.32)	51.37 (51.59)	5.05 (4.82)	-	-
$p\text{-}CNC_6H_4$	238-242	26.87 (28.46)	49.34 (46.08)	3.25 (3.39)	-	5.99 (6.72)
$o\text{-}CH_3C_6H_4$	142-144	28.31 (28.32)	51.88 (51.59)	4.91 (4.82)	-	-
CH_2Cl	165-167 ^a	35.52 (35.35)	b	b	b	-
$C_6H_5^c$	116-118.5	23.10 (23.04)	60.64 (60.62)	4.12 (3.92)	-	-

^a Lit.¹⁴³ 162-165 $^{\circ}$. ^b Not analyzed. ^c For $(C_6H_5)_2Sn(OOC_6H_5)_2$

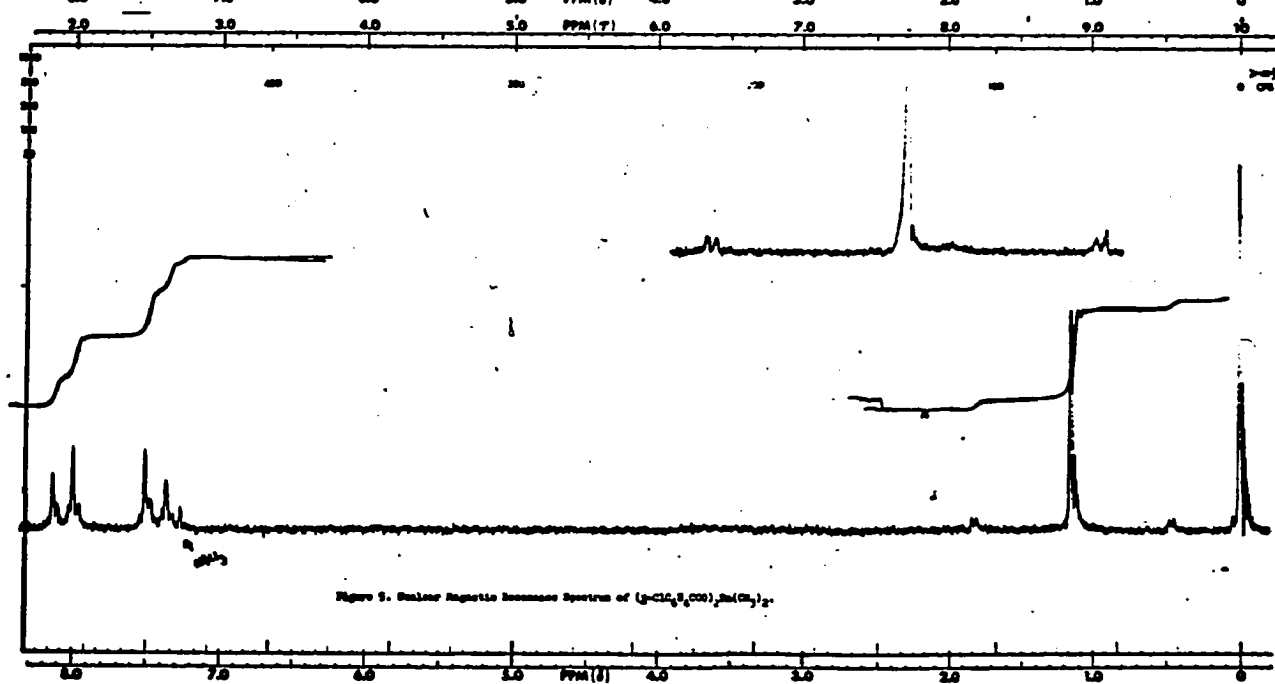
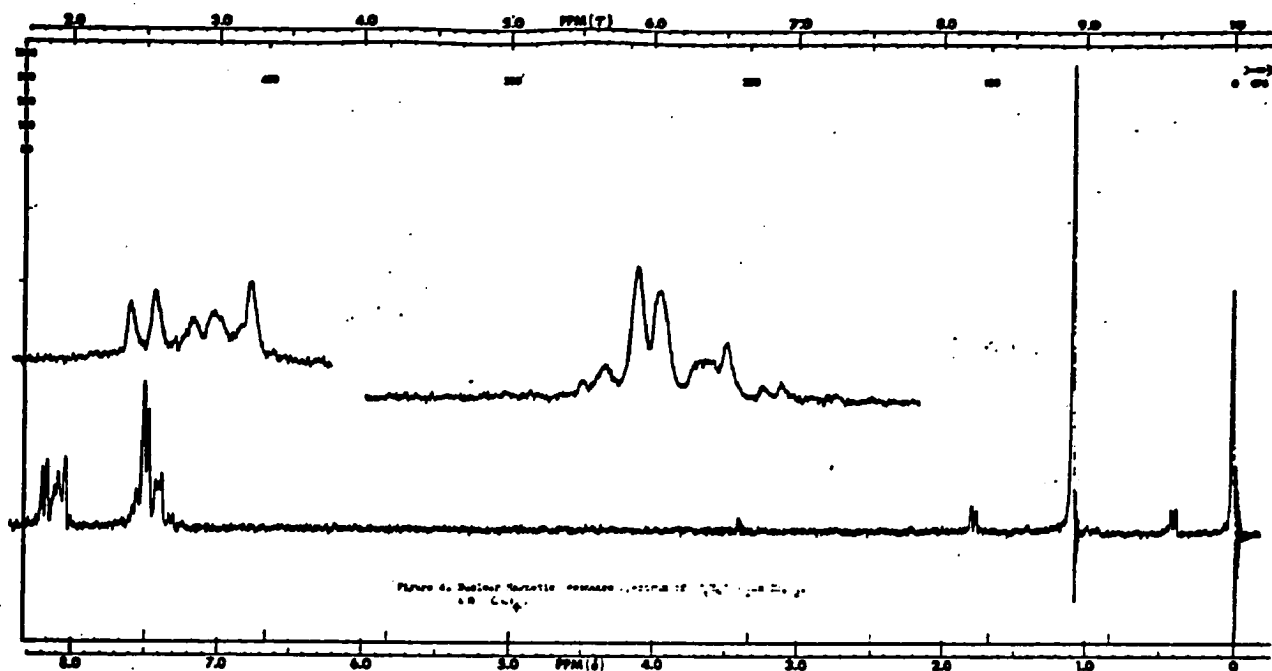
TABLE XIII

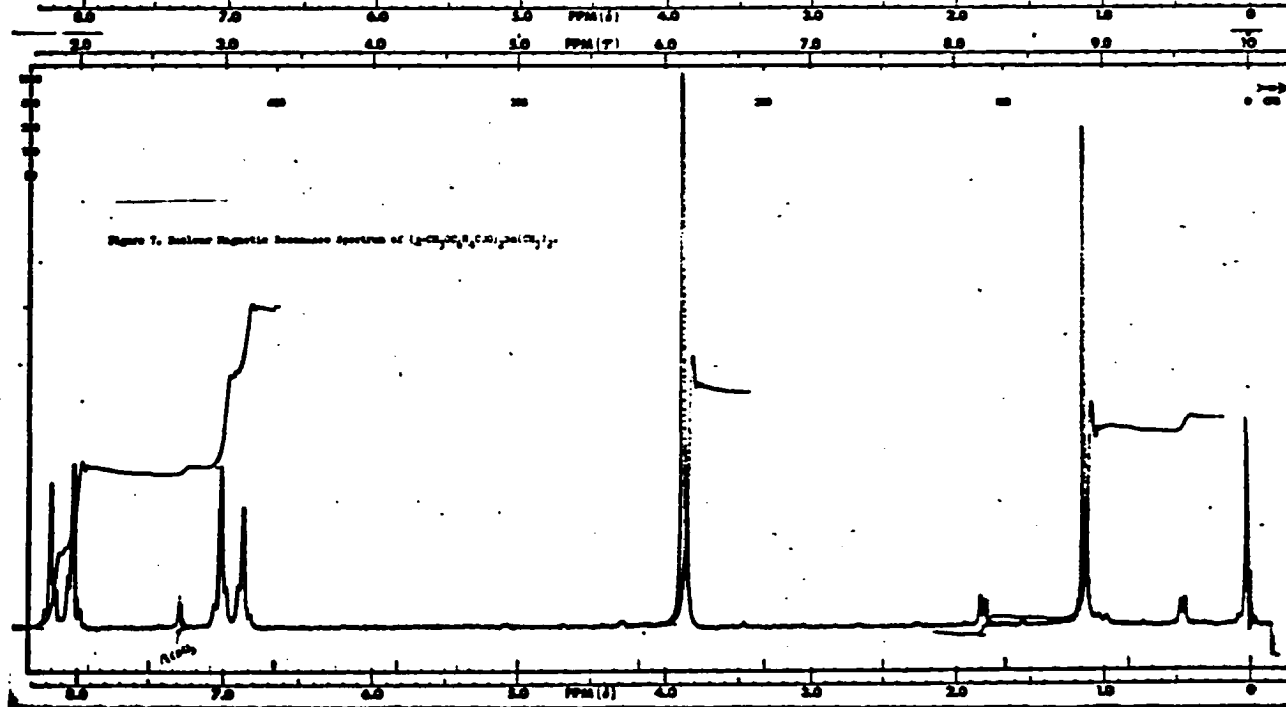
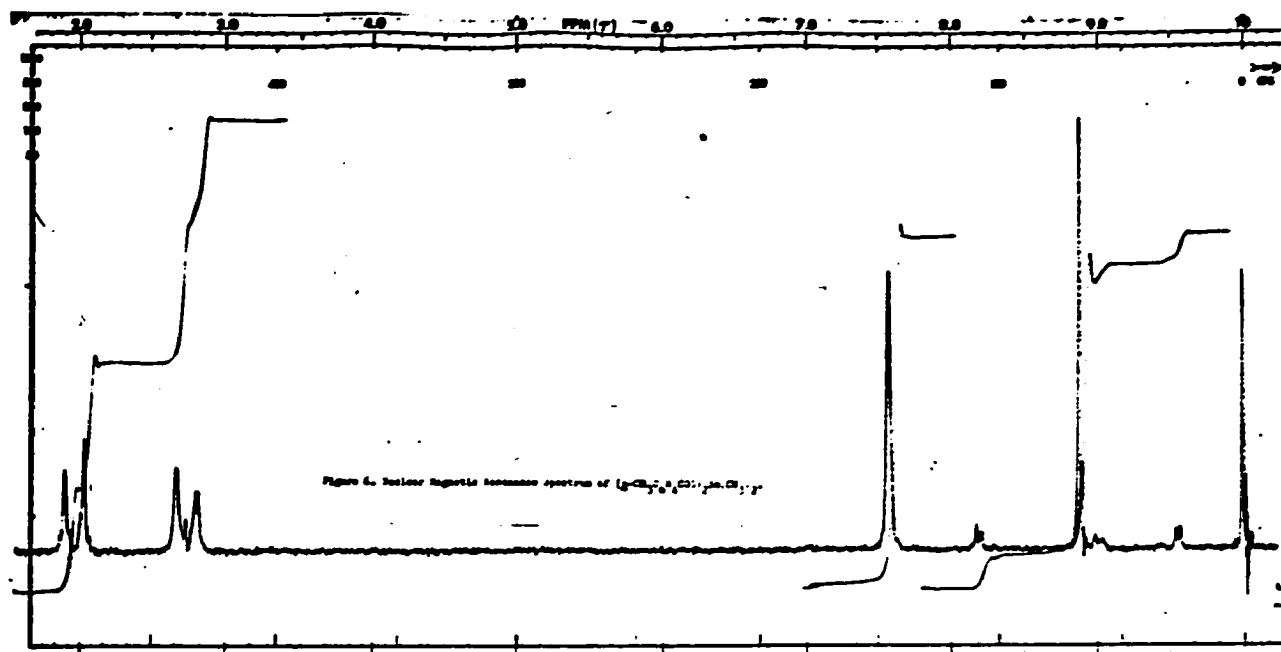
Molecular Weight Data for $(\underline{p}\text{-XC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2^a$

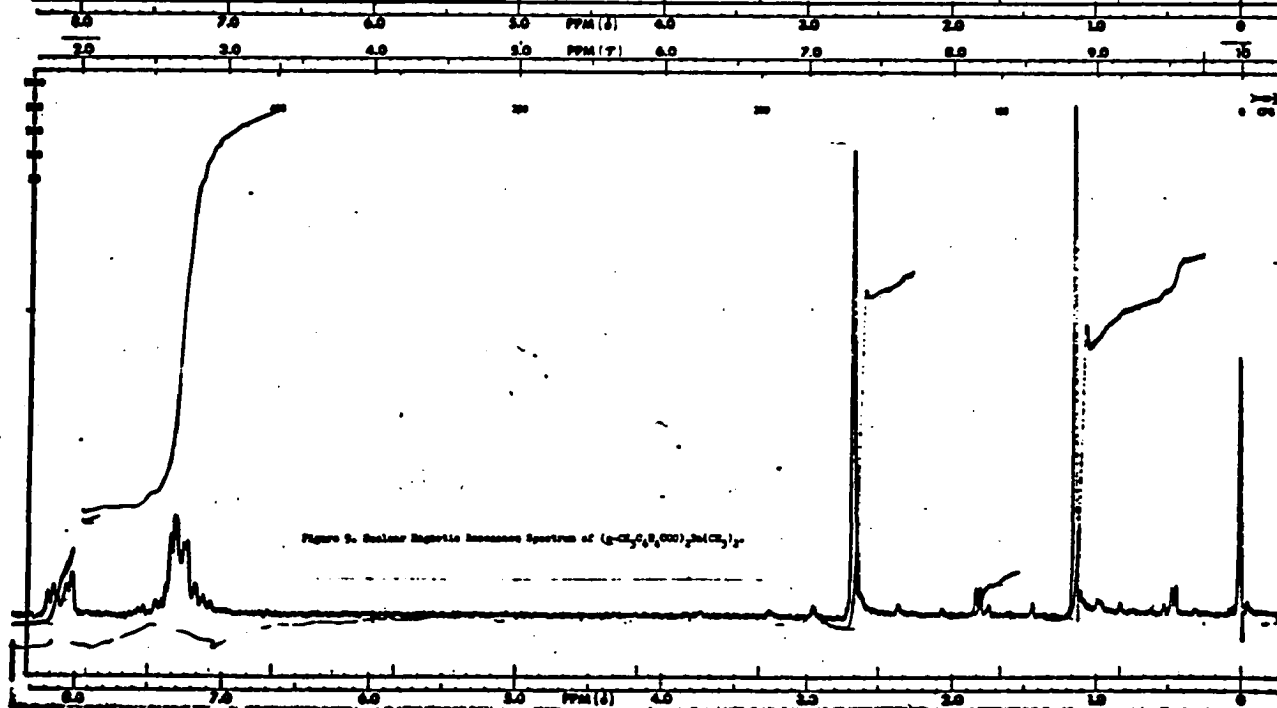
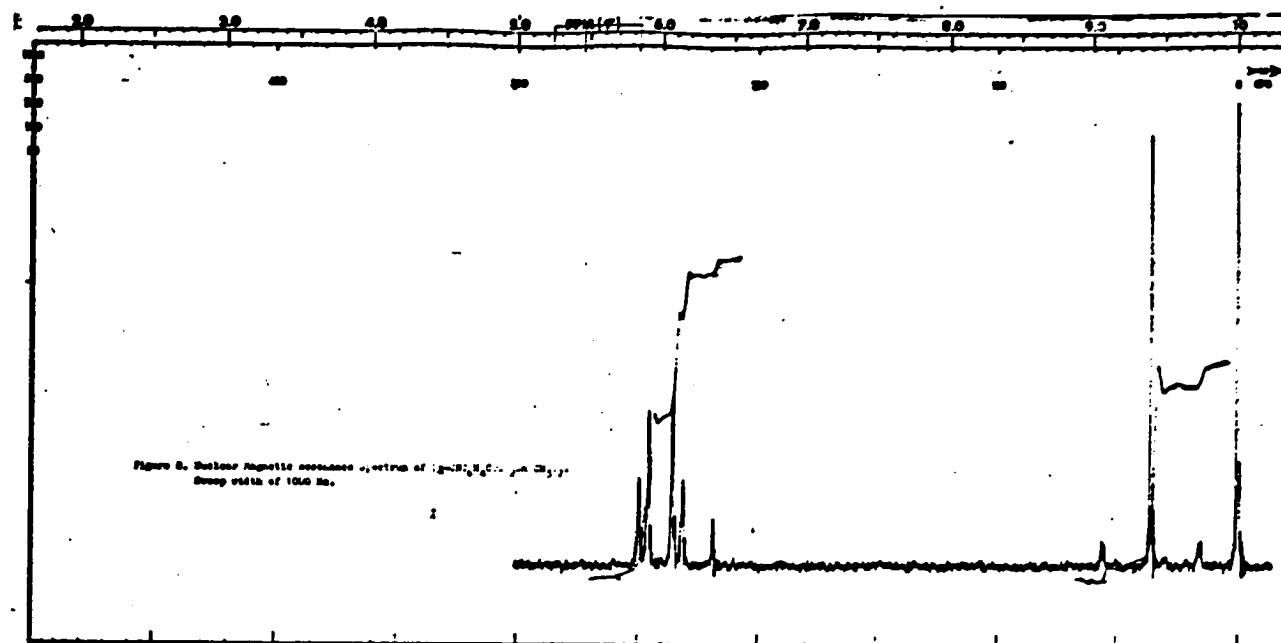
X	Concentration (mg/ml)	Molecular Weight	Degree of Association
H	infinite dilution	373	0.95
	4	394	1.01
	6	404	1.03
	10	448	1.15
	14	469	1.20
Cl	infinite dilution	456	0.99
	4	478	1.04
	6	518	1.13
	10	560	1.22
	14	572	1.25
CH ₃	infinite dilution	410	0.98
	4	448	1.07
	6	488	1.16
	10	535	1.28
	14	607	1.47
CH ₃ O	infinite dilution	430	0.96
	4	469	1.06
	6	478	1.08
	10	518	1.15
	14	554	1.23
CN ^b	infinite dilution	431	1.03
	4	462	1.11
	6	525	1.26
	10	540	1.30
	14	578	1.39

^aIn benzene except where noted.

^bIn Chloroform.







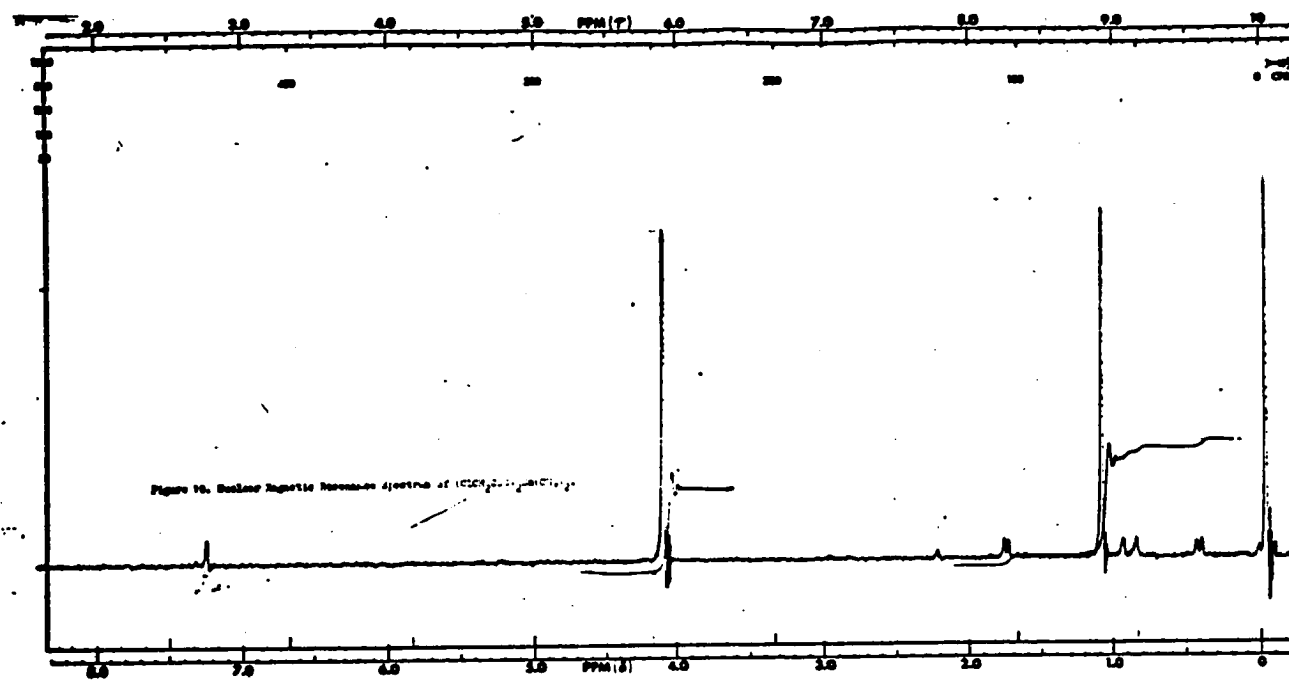


TABLE XIV

Proton Magnetic Resonance Spectra of

$(\text{CH}_3)_2\text{Sn}(\text{OOCR})_2$ in CDCl_3 at 40°C .

R	$J(^{117}\text{Sn}-\text{C}-\text{H})$ (Hz)	$J(^{119}\text{Sn}-\text{C}-\text{H})$ (Hz)	$\tau(\text{Sn}-\text{CH}_3)$ (ppm)	τ -Substituent (ppm)
C_6H_5	80.2	84.0	8.85	-
$\text{p-ClC}_6\text{H}_4$	78.7	82.5	8.87	-
$\text{p-NH}_2\text{C}_6\text{H}_4^a$	81.7	85.5	8.78	5.09
$\text{p-NO}_2\text{C}_6\text{H}_4$	- - - - - Insoluble - - - - -			
$\text{p-CH}_3\text{OC}_6\text{H}_4$	80.1	83.8	8.88	6.14
$\text{p-CH}_3\text{C}_6\text{H}_4$	81.0	83.3	8.88	7.60
$\text{p-CNC}_6\text{H}_4$	79.1	82.8	8.81	-
$\text{o-CH}_3\text{C}_6\text{H}_4$	80.0	83.8	8.86	7.33
CH_3^b	78.9	82.5	9.09	7.99
CH_2Cl	78.2	81.5	8.88	5.87

^a In nitrobenzene. ^b In CCl_4 ; reference 20.

TABLE XV

Mössbauer Parameters for $(p\text{-XC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ ^a at 77°K.

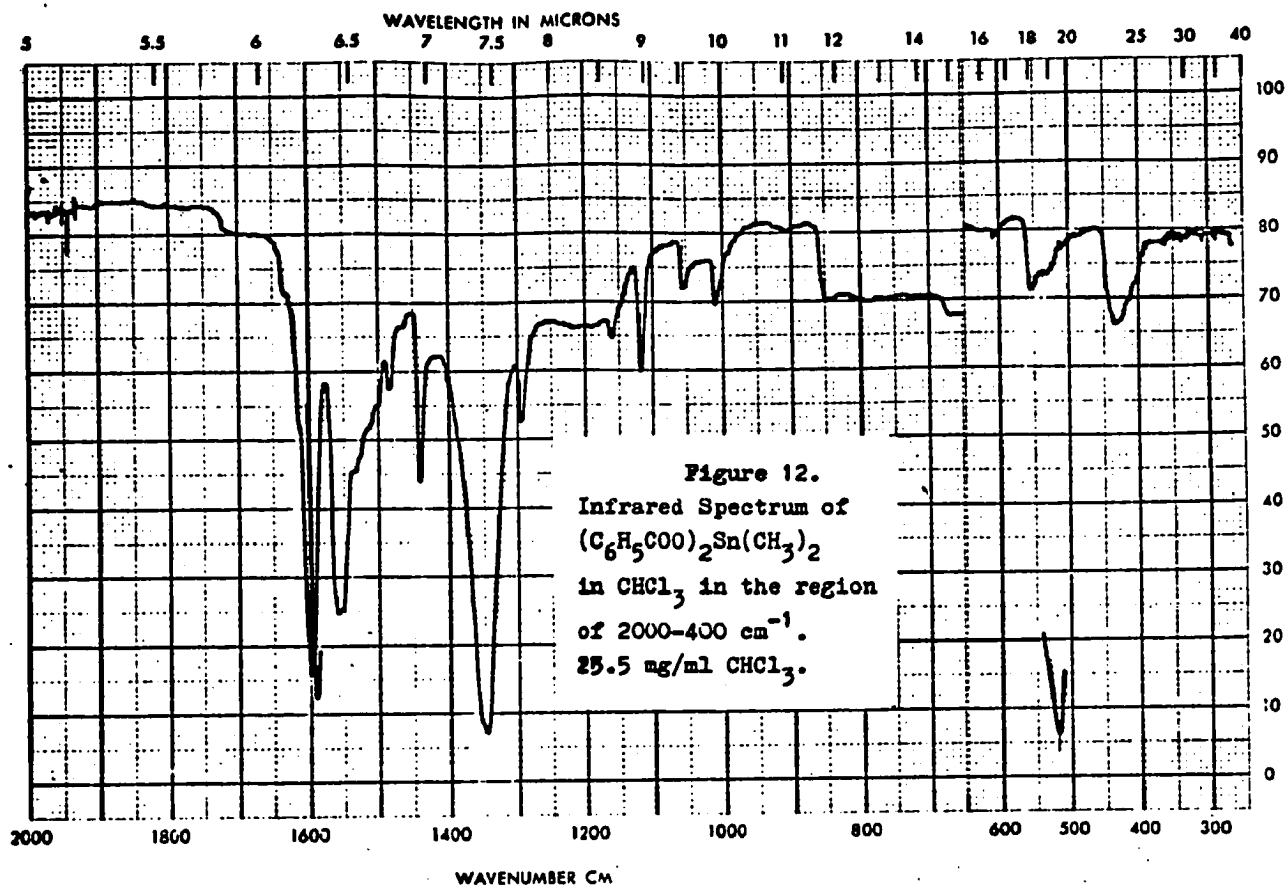
X	ΔE	δ ^b	Experimental Error
CN	3.98	1.42	± 0.008
H	3.80	1.38	± 0.006
Cl	3.84	1.35	± 0.009
NO ₂	3.70	1.35	± 0.006
CH ₃ ^o	3.56	1.28	± 0.007
CH ₃	3.34	1.18	± 0.009
NH ₂	3.27	1.21	± 0.008
CH ₃ ^c	3.41	1.28	± 0.005
CH ₂ Cl ^d	3.63	1.28	± 0.01

^a Data in mm/sec. ^b With respect to BaSnO₃ as source.

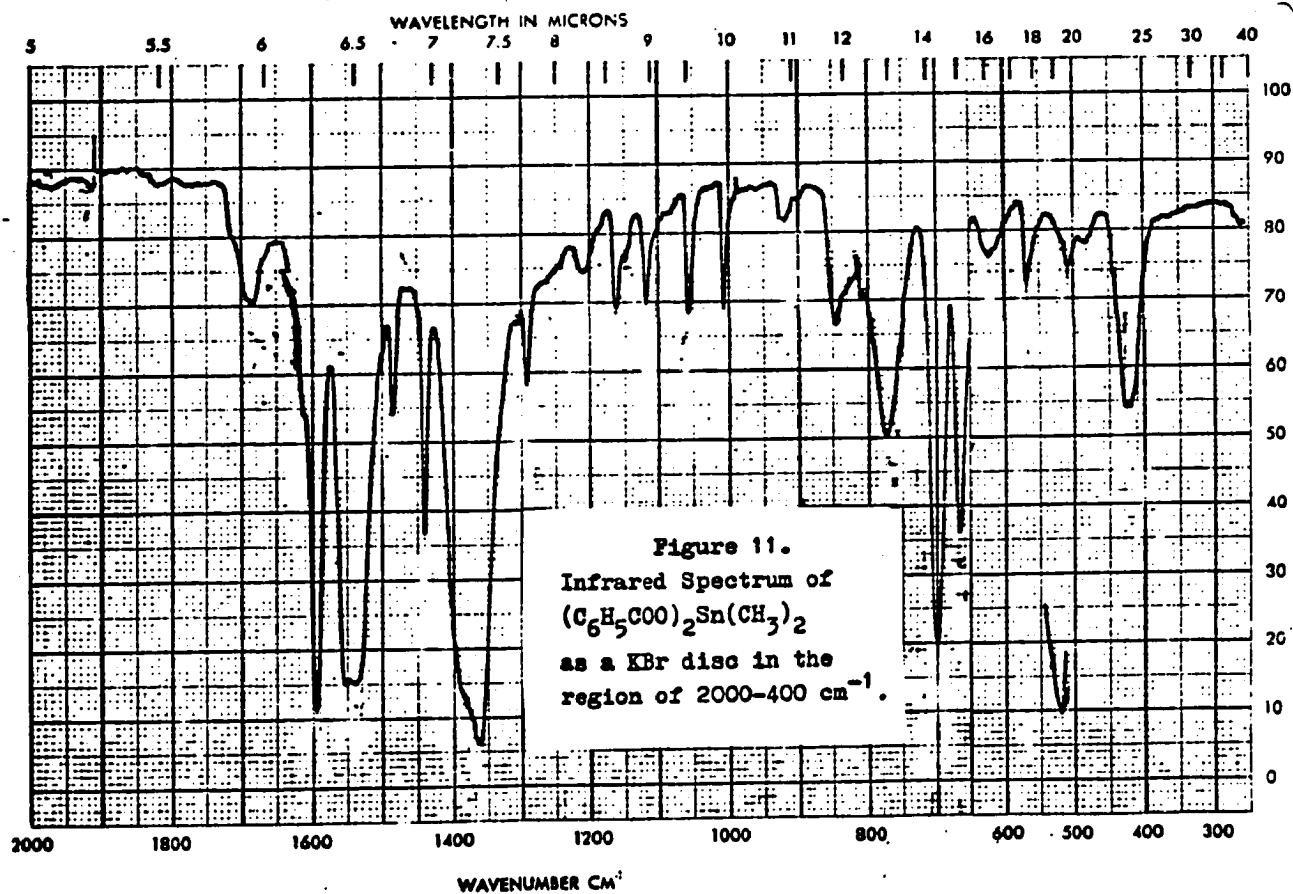
^c Ortho isomer. ^d For $(\text{CH}_3)_2\text{Sn}(\text{OOCCH}_2\text{Cl})_2$.

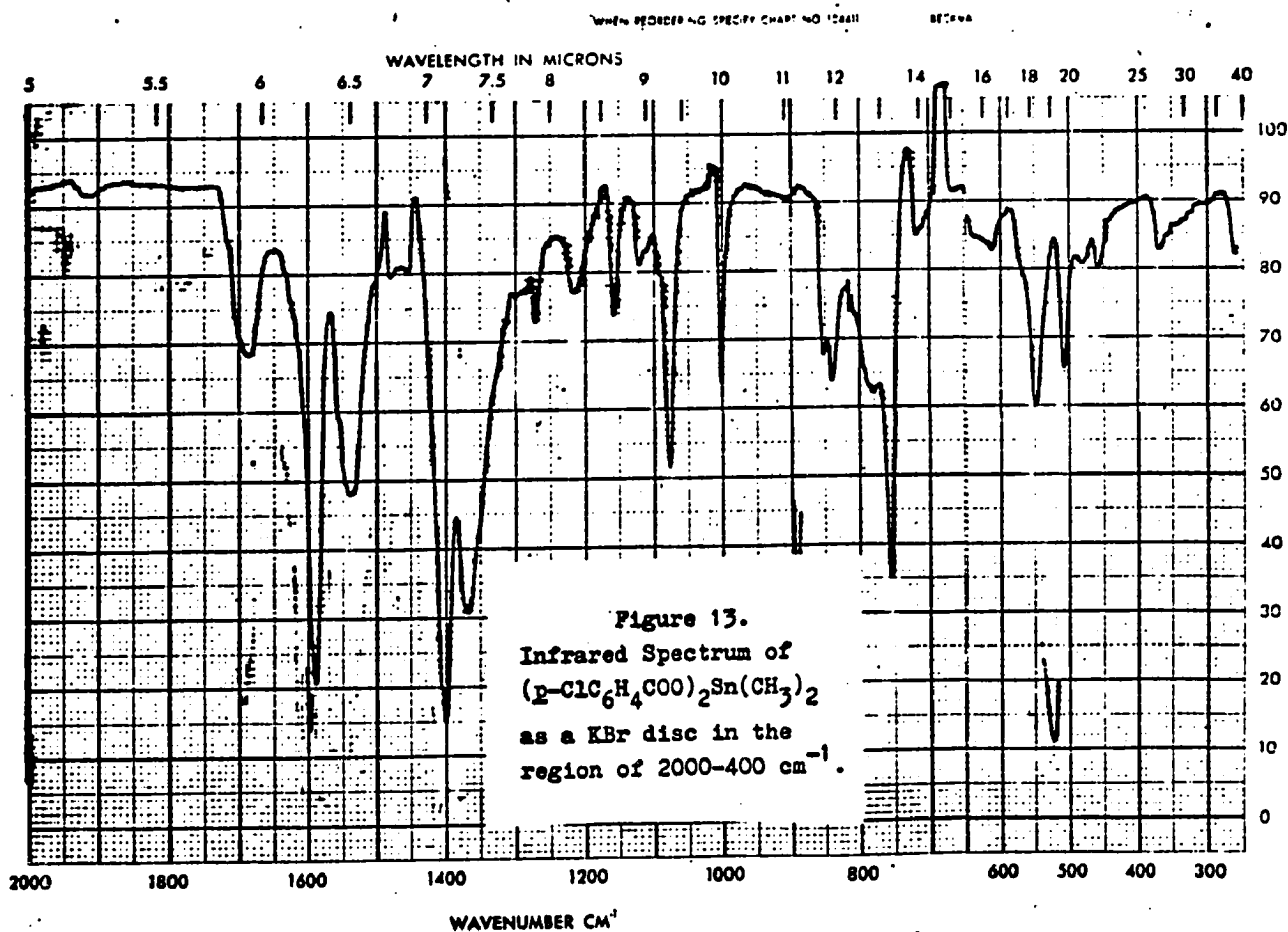
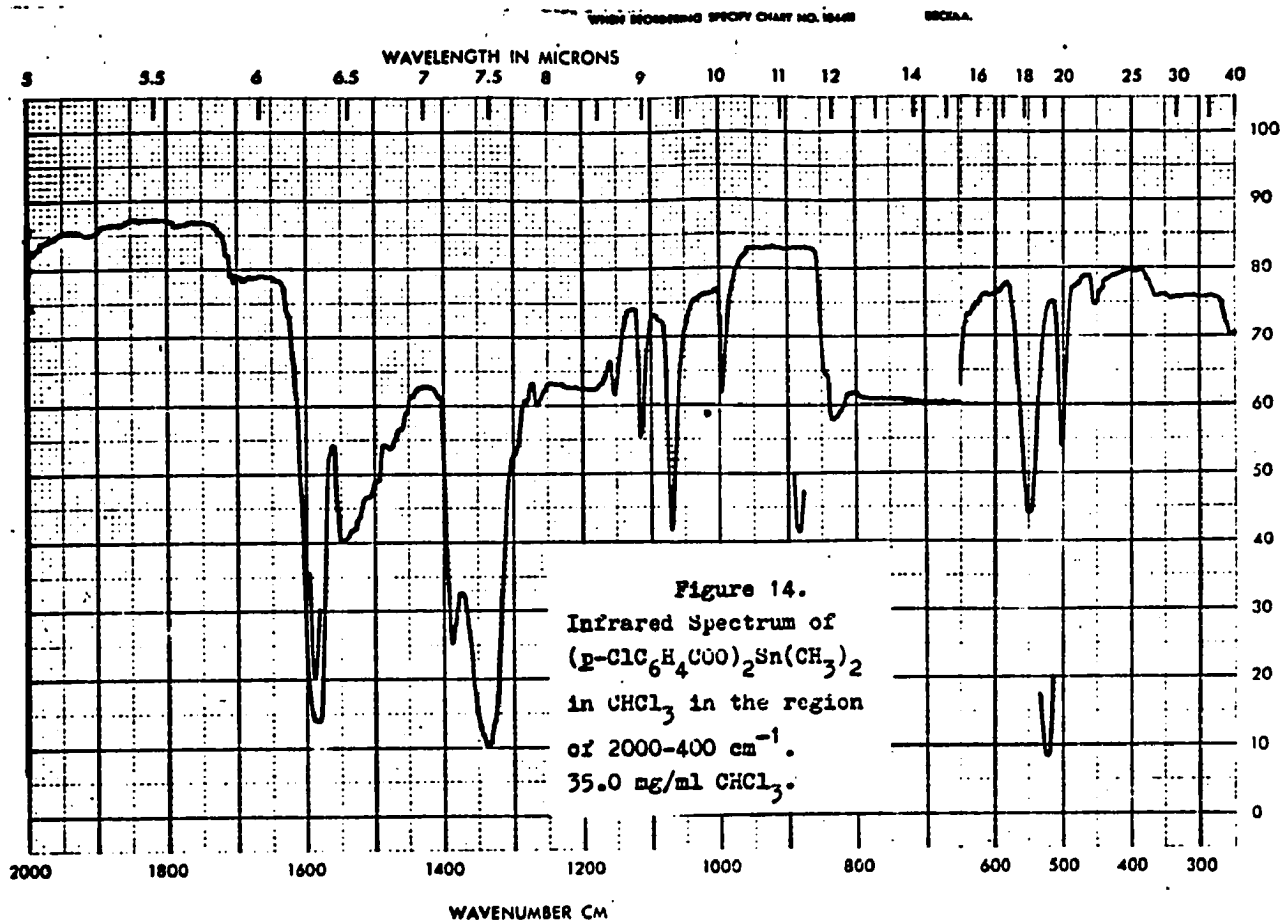
WHEN REORDERING SPECIFY CHART NO. 10448

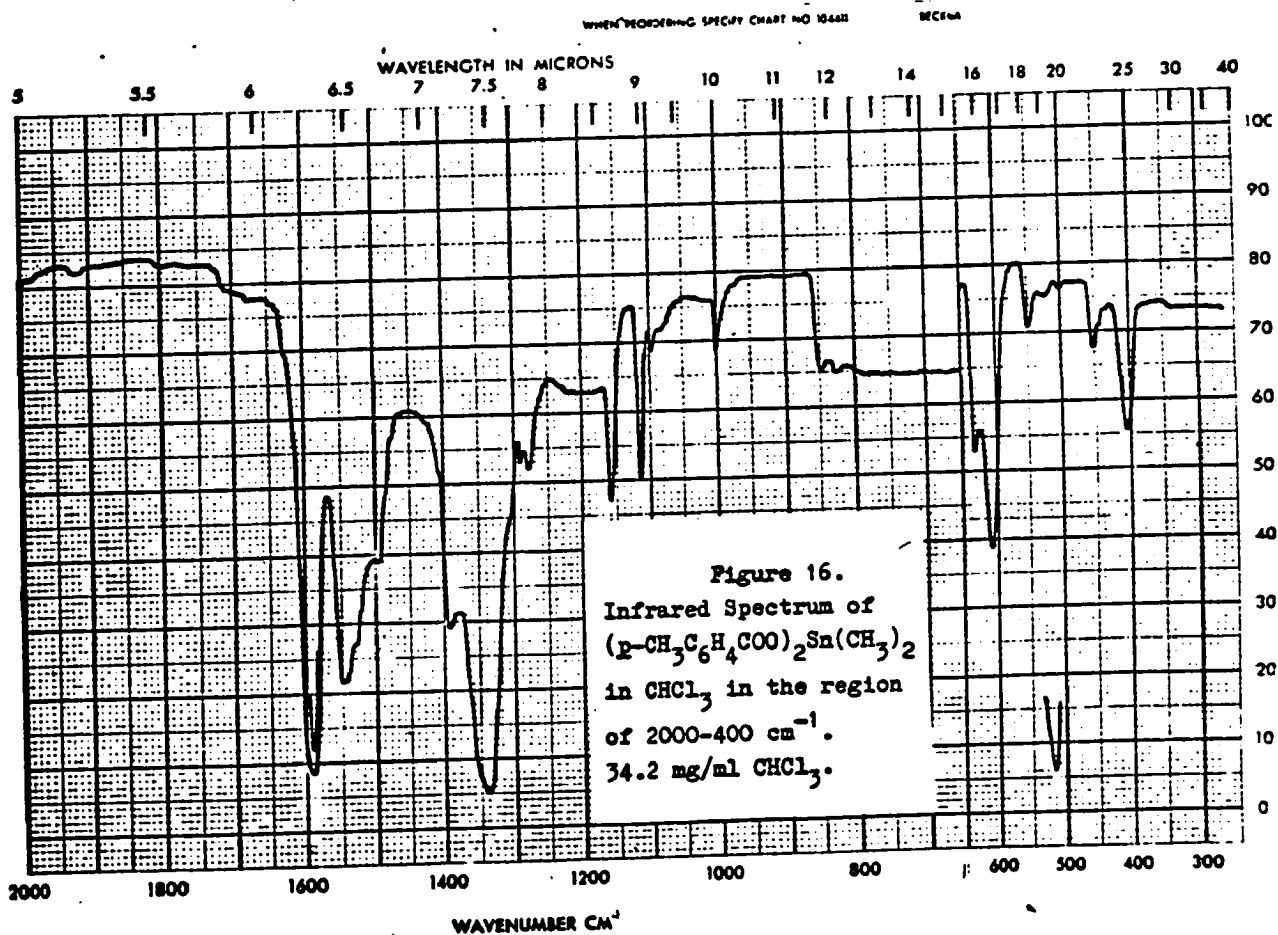
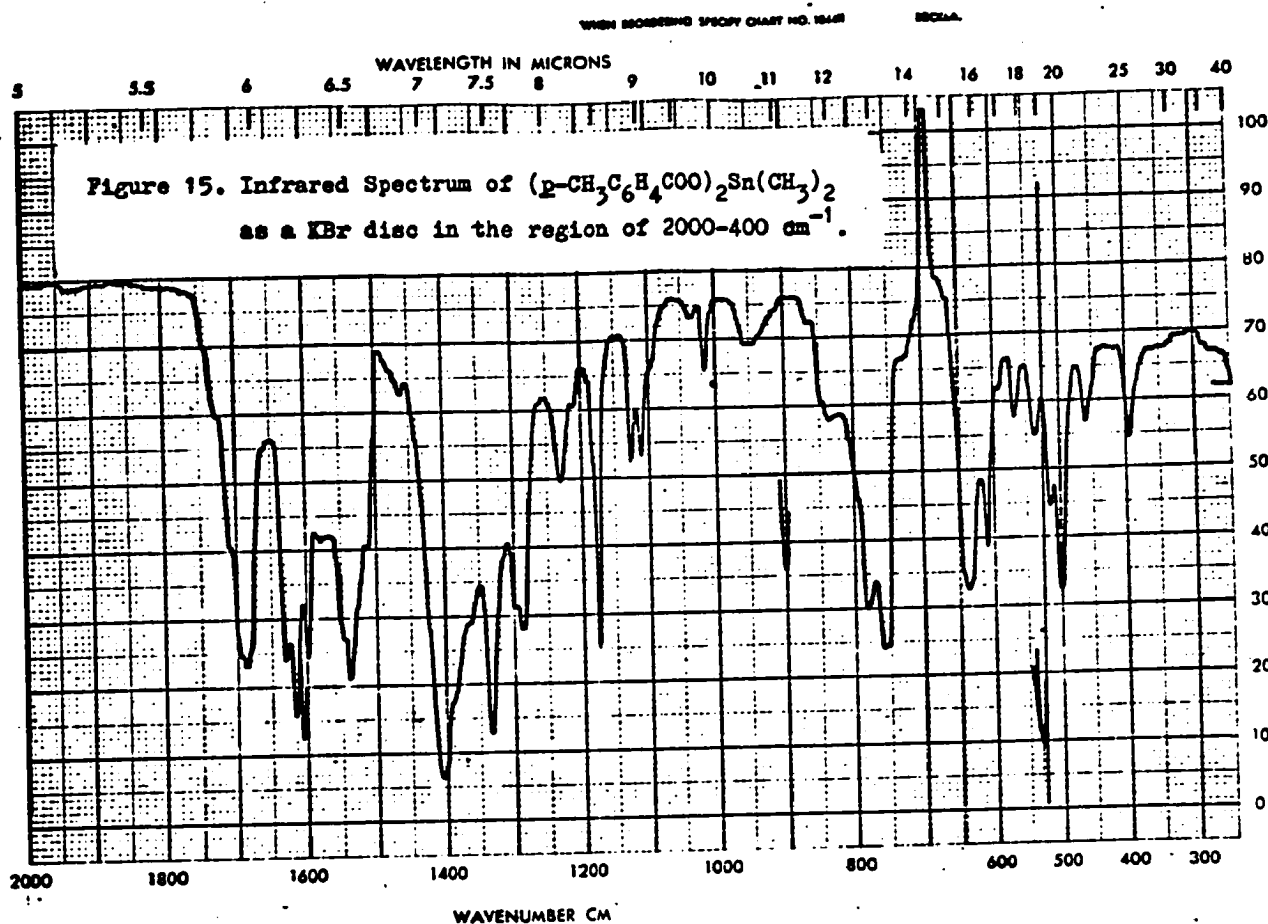
SPECTRA

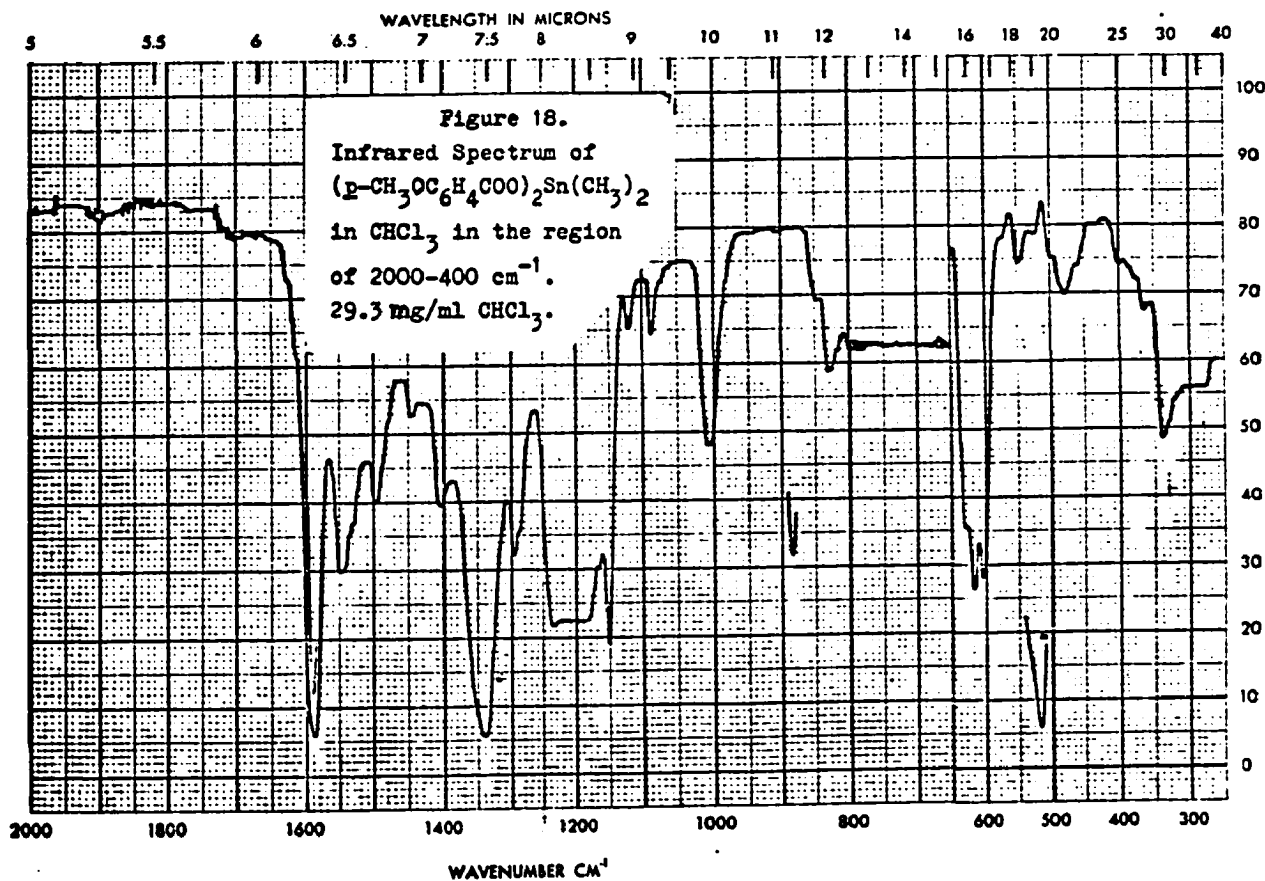
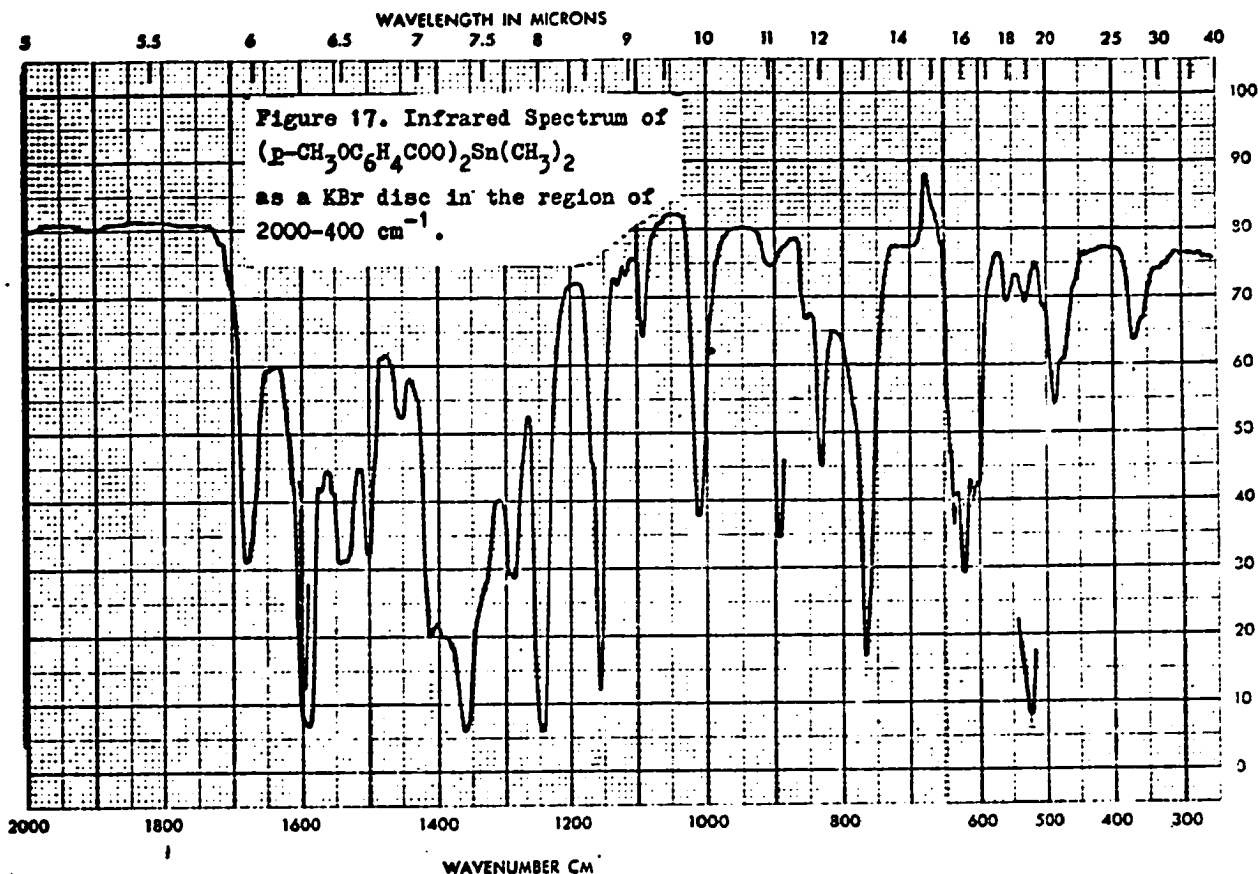


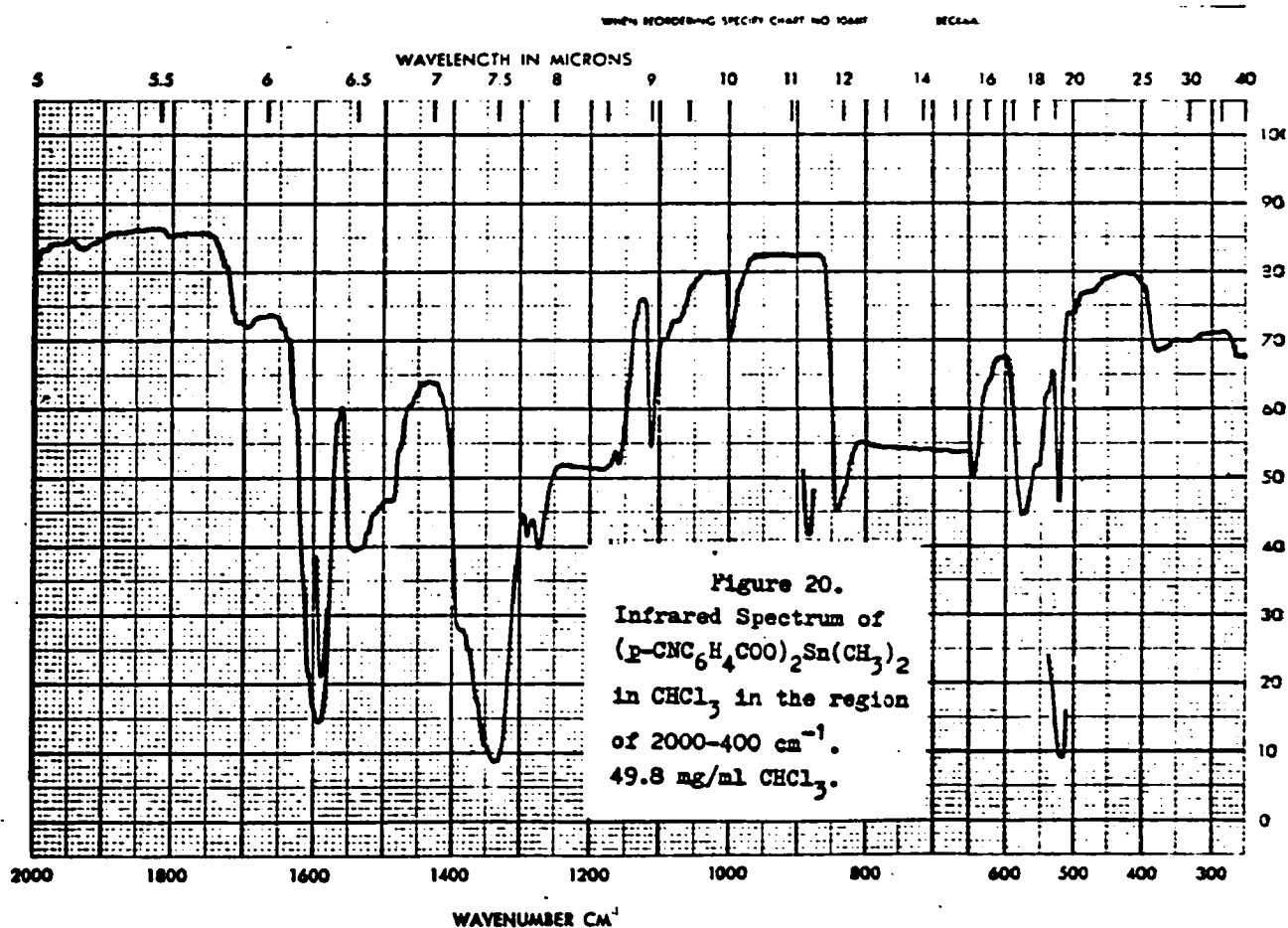
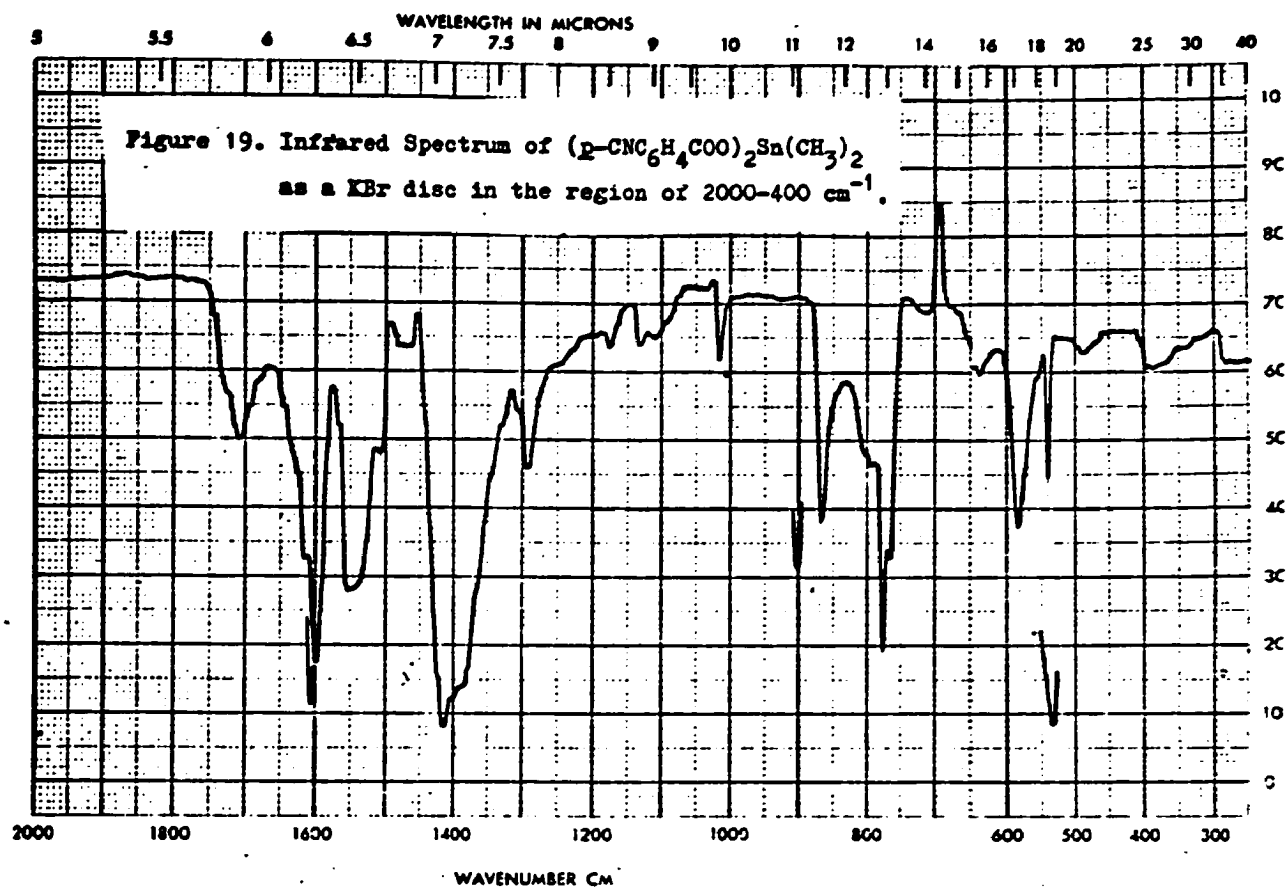
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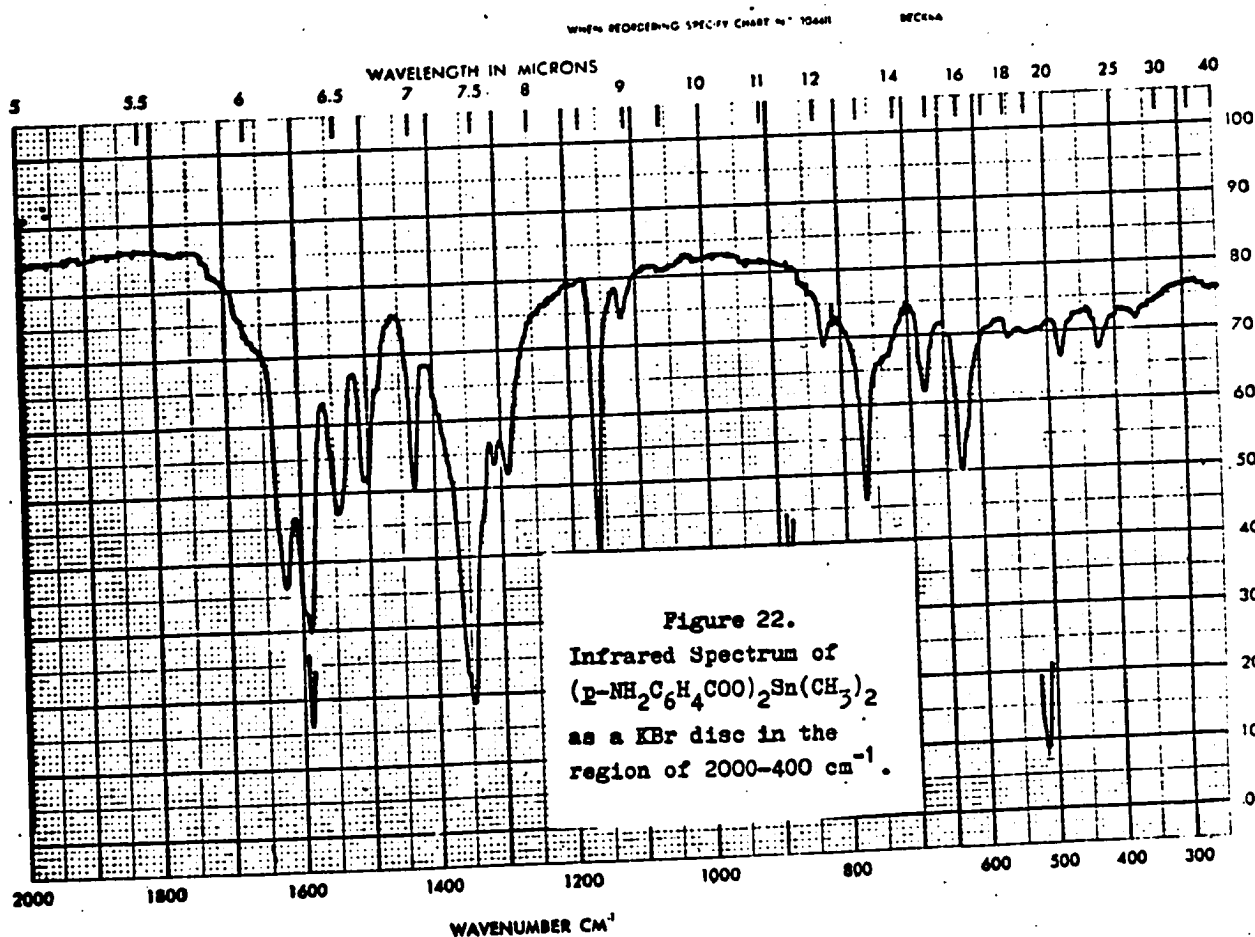
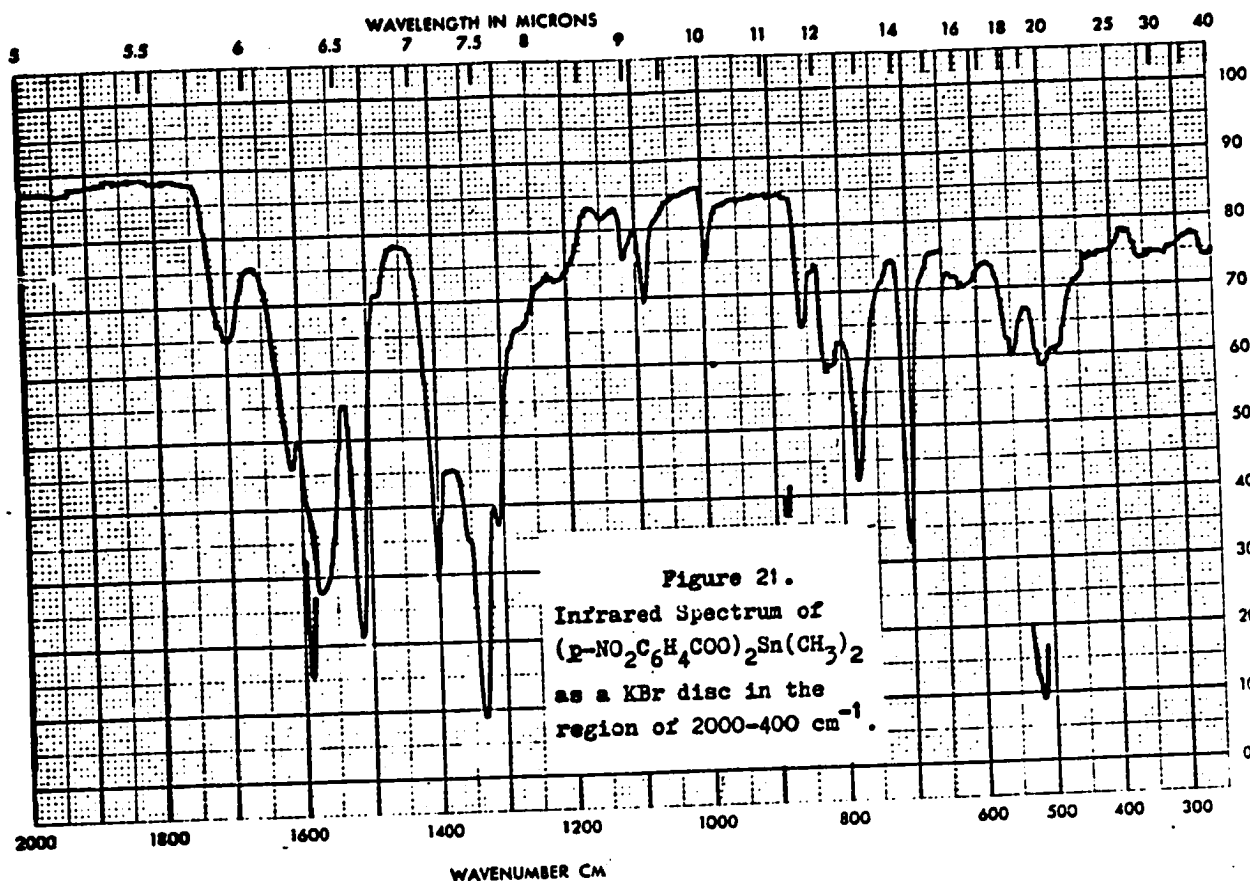






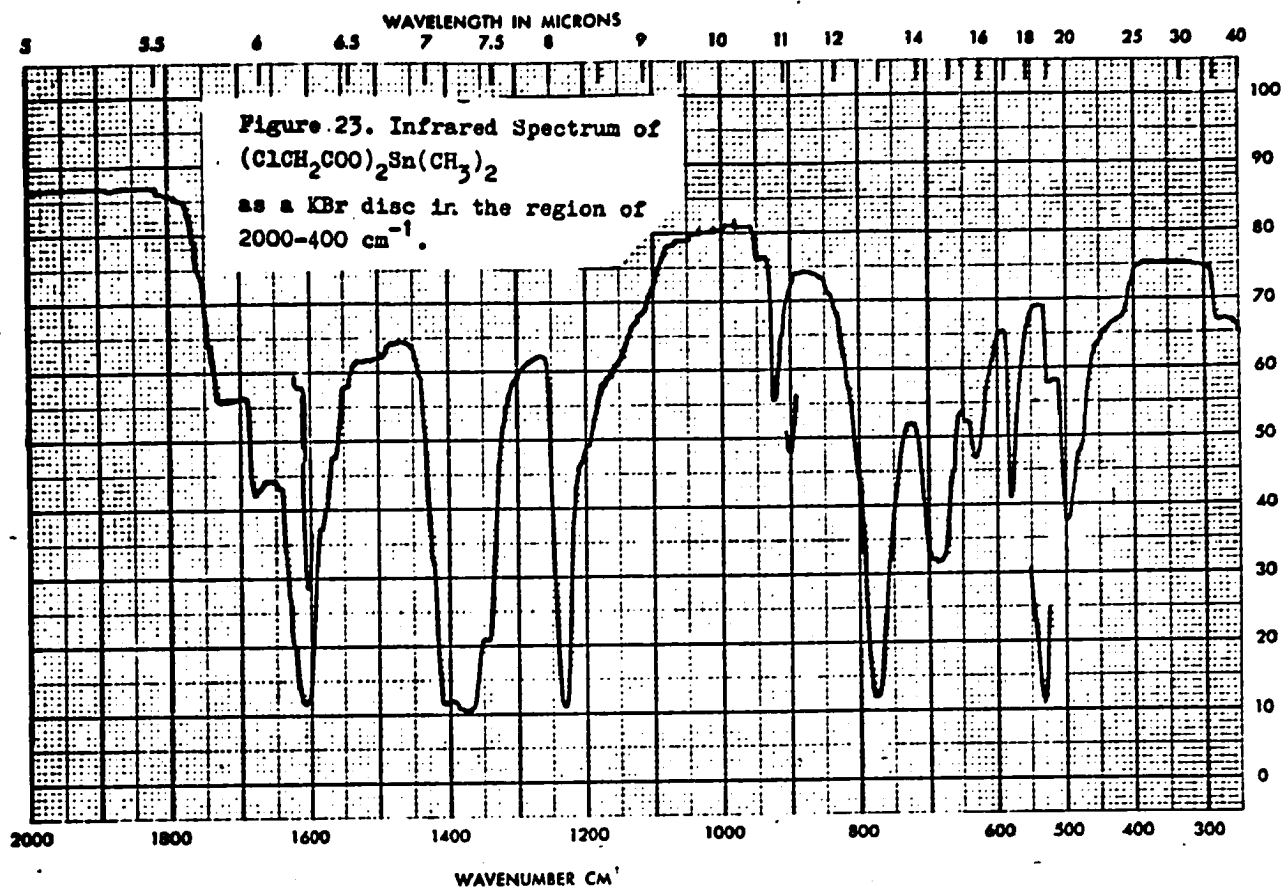






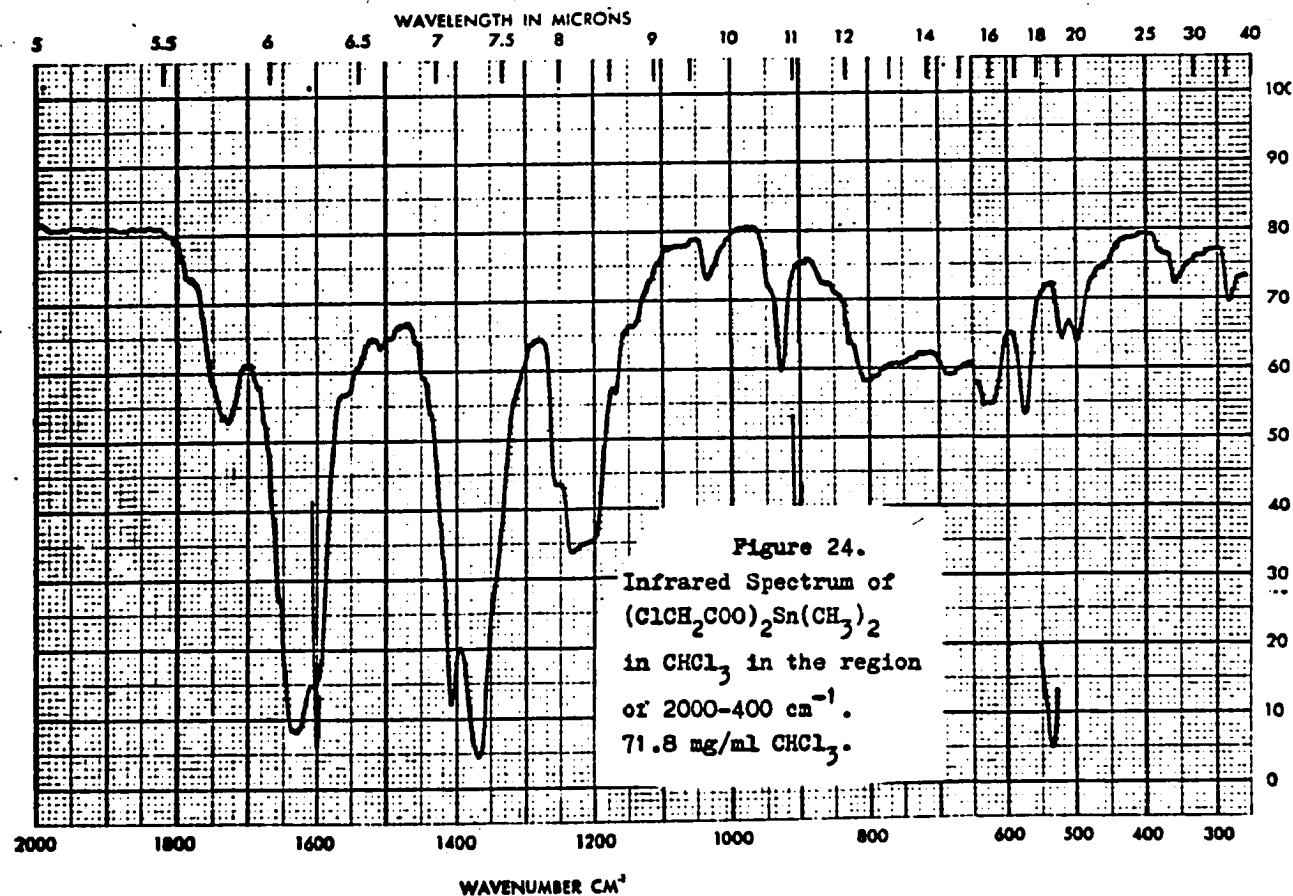
WHEN REORDERING, SPECIFY CHART NO. 10441

SPECTRA



WHEN REORDERING, SPECIFY CHART NO. 10441

SPECTRA



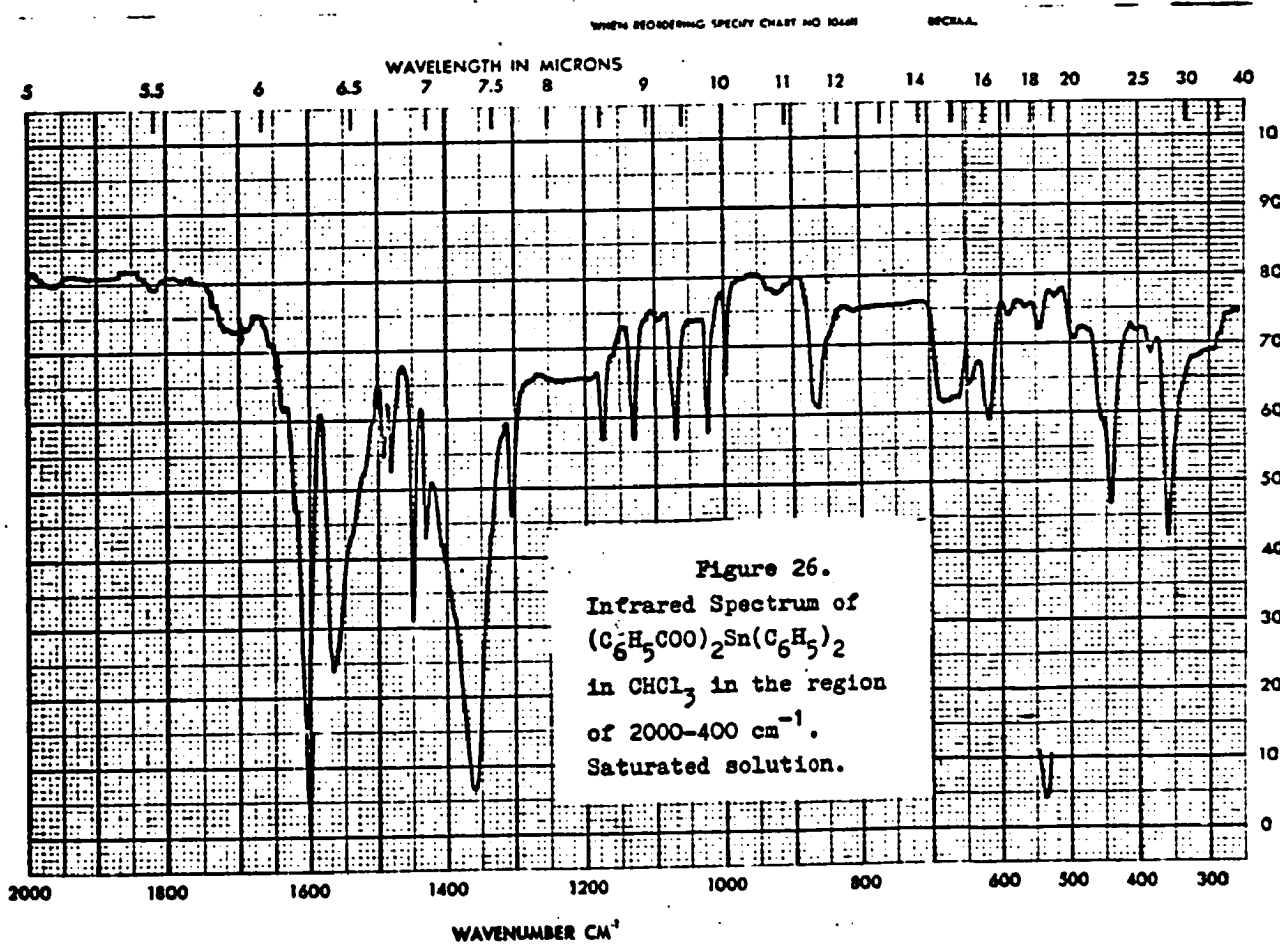
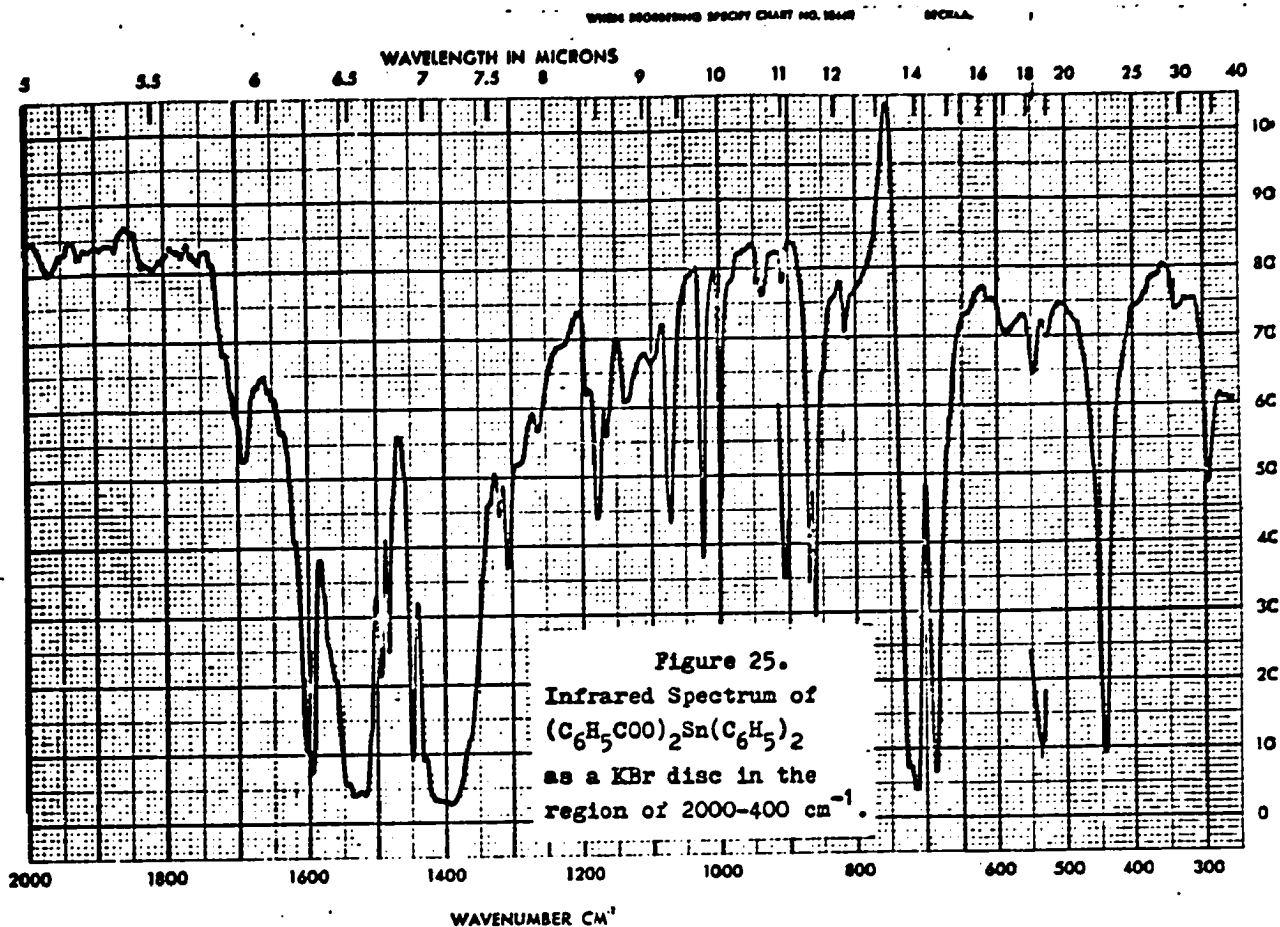


TABLE XVI

Sn-C Stretching Frequencies of
 $(\underline{p}\text{-XC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ (cm.^{-1})

X	Asymmetric		Symmetric	
	<u>Solid</u> ^a	<u>Soln.</u> ^b	<u>Solid</u> ^a	<u>Soln.</u> ^b
H	589 vw	572 vw	539 vw, sh	526 vw
CH ₃ O	579 w	568 vw	529 w, sh	520 vw, sh
NO ₂	571 w	-	528 w	-
NH ₂	575 w	-	524 w	-
Cl	570 w	568 m	530 w	522 w
CH ₃	576 w	569 vw	523 m	523 vw
CN	588 m	579 w, sh	525 w	522 vw, sh

^a KBr disc or nujol mull. ^b CHCl₃ or C₆H₆.

TABLE XVII

COO Stretching Frequencies of NaOOCR (cm. ⁻¹) ^a				
R	Asym.	Sym.	Separation	Reference
C ₆ H ₅	1547	1407	140	This work
<u>p</u> -CH ₃ OC ₆ H ₄	1530	1401	129	This work
<u>p</u> -NH ₂ C ₆ H ₄	1532	1391	141	This work
<u>p</u> -NO ₂ C ₆ H ₄	1584	1402	182	This work
<u>p</u> -CNC ₆ H ₄	1548	1399	149	This work
<u>p</u> -ClC ₆ H ₄	1537	1394	143	This work
<u>p</u> -CH ₃ C ₆ H ₄	1550	1416	134	This work
H	1592	1370	222	144
CH ₃	1576	1440	136	126
ClCH ₂	1598	1418	180	126
Cl ₂ CH	1646	1395	241	126
Cl ₃ C	1672	1352	320	126
C ₂ H ₅	1560	1415	145	145
C ₁₁ H ₂₃	1560	1415	145	145

^a Solid state as KBr disc, Nujol mull or capillary film.

TABLE XVIII

COO Stretching Frequencies of $(\text{CH}_3)_2\text{Sn}(\text{OOCR})_2$ (cm^{-1})

R	Solid ^a		Solution ^b	
	<u>Asym.</u>	<u>Sym.</u>	<u>Asym.</u>	<u>Sym.</u>
C_6H_5	1560 1547	1371	1568	1358
$\text{p-CH}_3\text{OC}_6\text{H}_4$	1549 1538	1371	1559	1351
$\text{p-NH}_2\text{C}_6\text{H}_4$	1545	1360	Insoluble	
$\text{p-NO}_2\text{C}_6\text{H}_4$	1583	1363	Insoluble	
$\text{p-CNC}_6\text{H}_4$	1546	1412 1366	1552	1346
$\text{p-ClC}_6\text{H}_4$	1544	1372	1555	1349
$\text{p-CH}_3\text{C}_6\text{H}_4$	1547	1401	1558	1351
CH_3^c	1600 1560	1438 1374	1607	1433 1380
ClCH_2	1611	1408 1375	1633	1361
C_2H_5^c	1600 1570	1422 1376	1607	1425 1378

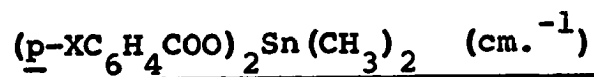
^aKBr disc except Nujol mulls for $\text{R} = \text{CH}_3$.

^bIn CHCl_3 except in C_6H_{12} for $\text{R} = \text{CH}_3$ and C_2H_5 .

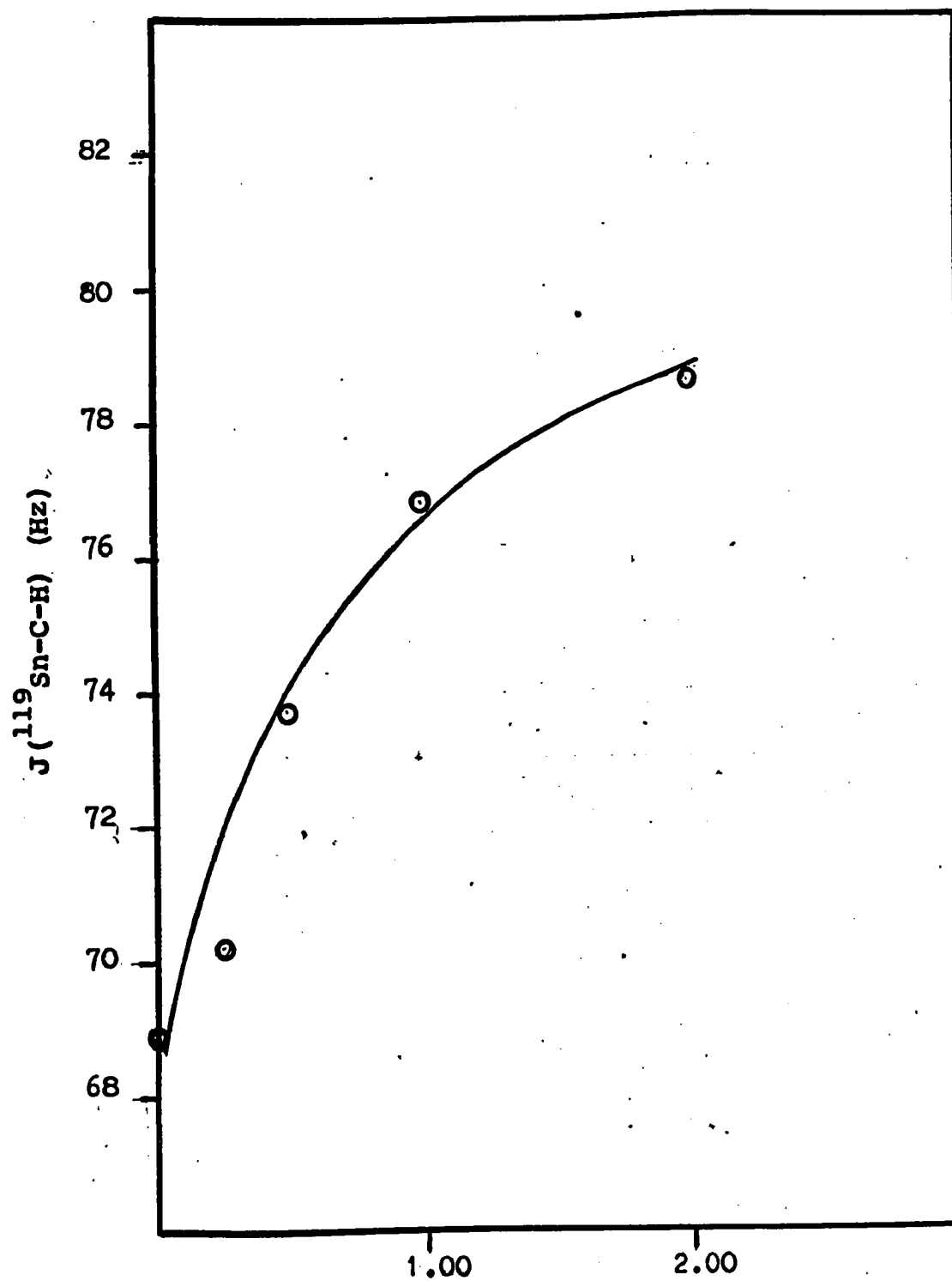
^cReference 20.

TABLE XIX

Sn-O Stretching Frequencies of



X	Solid	Solution
H	420	423
CH ₃ O	389	386
NO ₂	378	-
NH ₂	440	-
Cl	390	383
CH ₃	403	425
CN	391	389



Moles $(p\text{-CH}_3\text{OC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ / Moles $(\text{CH}_3)_2\text{SnCl}_2$

Figure 27. Variation of J with varying relative concentrations of dimethyltin bis(p-methoxybenzoate) and dimethyltin dichloride in CDCl_3 .

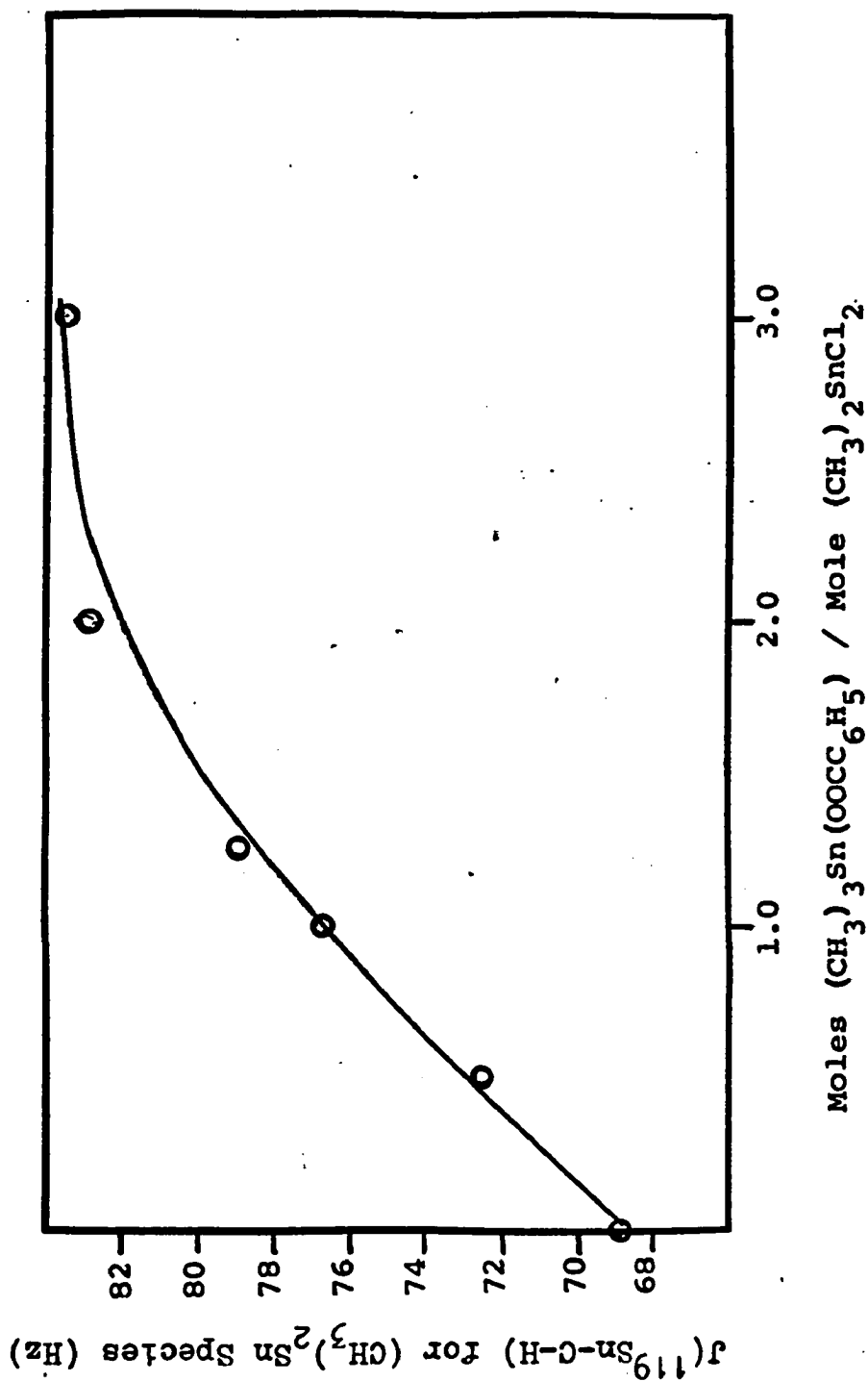


Figure 28. Variation of J for $(\text{CH}_3)_2\text{Sn}$ species with varying relative concentrations of $(\text{CH}_3)_3\text{Sn}(\text{OOCC}_6\text{H}_5)_3$ and $(\text{CH}_3)_2\text{SnCl}_2$ in CDCl_3 .

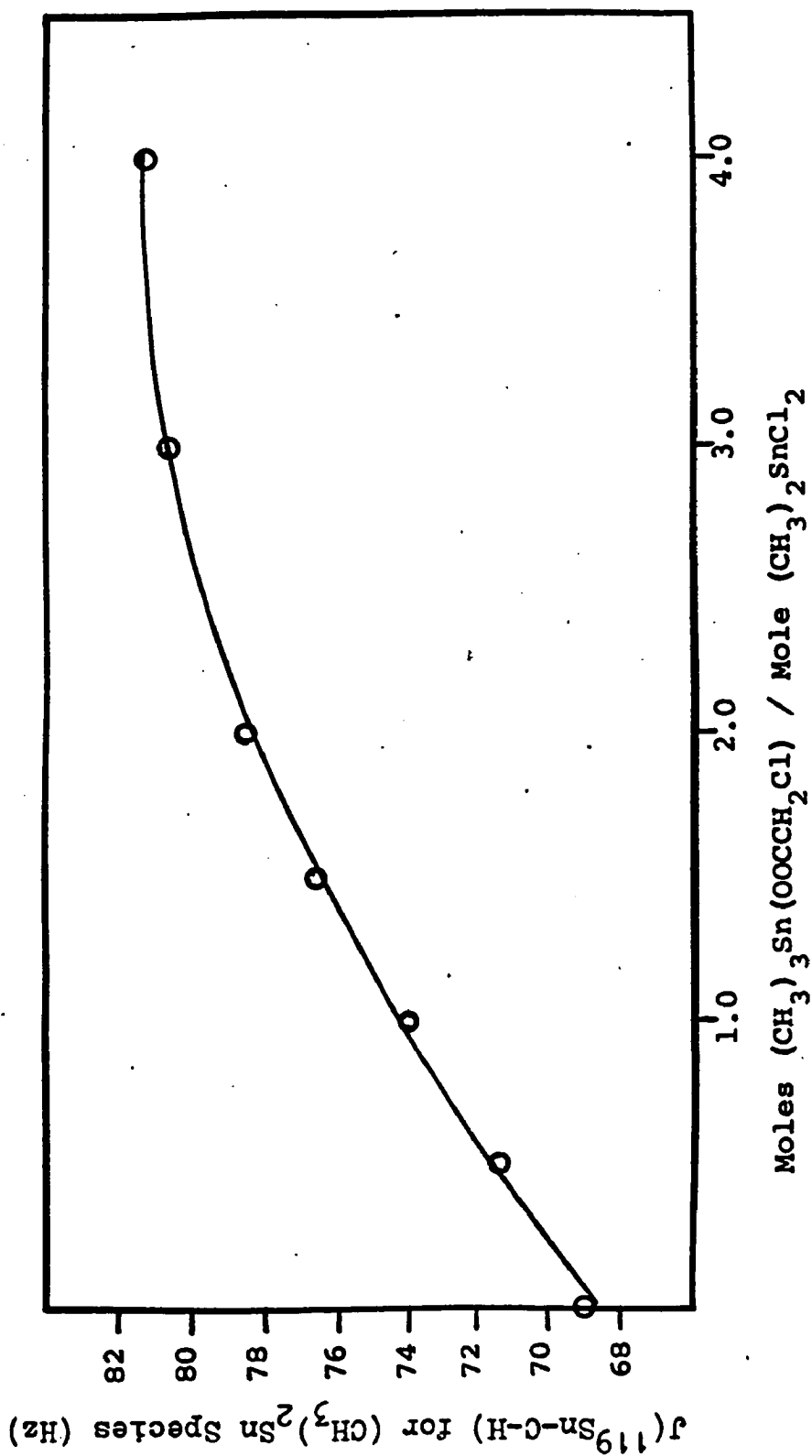


Figure 29. Variation of J for $(\text{CH}_3)_2\text{Sn}$ species with relative concentrations of $(\text{CH}_3)_3\text{Sn}(\text{OOCCH}_2\text{Cl})$ and $(\text{CH}_3)_2\text{SnCl}_2$. Concentration of $(\text{CH}_3)_2\text{SnCl}_2$ kept constant at 35.6 mg / ml CDCl_3 .

TABLE XX

NMR Evidence for Exchange Between Methyltin Chlorides
and Methyltin Benzoates^a

Composition of Mixture	Mole Ratio	SnC ₂ Species		SnC ₃ Species	
		τ^b	J^c	τ^b	J^c
$R_2SnCl_2 : R_3SnCl_3^d$	1:1	8.78	69.2	9.33	58.8
$R_2SnCl_2 : R_3Sn(OOCR')^e$	1:1	8.83	77.5	9.34	59.2
$R_2SnCl_2 : R_3Sn(OOCR')$	1:2	8.86	82.9	9.34	59.6
$R_3SnCl : R_3Sn(OOCR')$	1:1	-	-	9.36	59.0
$R_3SnCl : R_2Sn(OOCR'')^f_2$	1:1	8.88	83.7	9.35	59.2
R_2SnCl_2	Pure Compound	8.80	68.9	-	-
R_3SnCl	Pure Compound	-	-	9.35	57.8
$R_3Sn(OOCR')$	Pure Compound	-	-	9.37	58.7
$R_2Sn(OOCR'')_2$	Pure Compound	8.88	83.8	-	-

^a In CHCl₃ or CDCl₃. ^b TMS = 10 ppm. ^c In Hz. ^d R = CH₃.

^e R' = C₆H₅. ^f R'' = p-CH₃OC₆H₄.

TABLE XX

NMR Evidence for Exchange Between Methyltin Chloridesand Methyltin Benzoates^a

Composition of Mixture	Mole Ratio	SnC ₂ Species		SnC ₃ Species	
		τ^b	J^c	τ^b	J^c
$R_2SnCl_2 : R_3SnCl_3^d$	1:1	8.78	69.2	9.33	58.8
$R_2SnCl_2 : R_3Sn(OOCR')^e$	1:1	8.83	77.5	9.34	59.2
$R_2SnCl_2 : R_3Sn(OOCR')$	1:2	8.86	82.9	9.34	59.6
$R_3SnCl : R_3Sn(OOCR')$	1:1	-	-	9.36	59.0
$R_3SnCl : R_2Sn(OOCR'')^f_2$	1:1	8.88	83.7	9.35	59.2
R_2SnCl_2	Pure Compound	8.80	68.9	-	-
R_3SnCl	Pure Compound	-	-	9.35	57.8
$R_3Sn(OOCR')$	Pure Compound	-	-	9.37	58.7
$R_2Sn(OOCR'')_2$	Pure Compound	8.88	83.8	-	-

^aIn CHCl₃ or CDCl₃. ^bTMS = 10 ppm. ^cIn Hz. ^dR = CH₃.

^eR' = C₆H₅. ^fR'' = p-CH₃OC₆H₄.

TABLE XXI

Results of Exchange Reactions

R	R'	R''	$\frac{\text{moles } R'_3\text{Sn}(\text{OOCR}'')}{\text{moles } R_2\text{SnCl}_2}$	Product
CH ₃	CH ₃	C ₆ H ₅	1	a
CH ₃	CH ₃	ClCH ₂	1	(CH ₃) ₂ SnCl(OOCH ₂ Cl)
CH ₃	n-C ₄ H ₉	C ₆ H ₅	1	(CH ₃) ₂ Sn(OOCC ₆ H ₅) ₂ ^b
CH ₃	C ₆ H ₅	CH ₃	1	(CH ₃) ₂ SnCl(OOCH ₃)
C ₆ H ₅	CH ₃	C ₆ H ₅	1	(C ₆ H ₅) ₂ SnCl(OOCC ₆ H ₅)
CH ₃	CH ₃	C ₆ H ₅	2	(CH ₃) ₂ Sn(OOCC ₆ H ₅) ₂
CH ₃	CH ₃	ClCH ₂	2	(CH ₃) ₂ Sn(OOCH ₂ Cl) ₂
CH ₃	C ₆ H ₅	CH ₃	2	(CH ₃) ₂ Sn(OOCH ₃) ₂ ^c
CH ₃	C ₆ H ₅	C ₆ H ₅	2	(CH ₃) ₂ Sn(OOCC ₆ H ₅) ₂ ^d
C ₆ H ₅	CH ₃	C ₆ H ₅	2	(C ₆ H ₅) ₂ Sn(OOCC ₆ H ₅) ₂

^a No pure compound isolated. see discussion. ^b Unexpected, see discussion. ^c Impure, see discussion. ^d Impure. Unable to isolate from the triphenyltin chloride.

TABLE XXII

Melting Points and Analysis of $R_2SnCl(OOCR')$

R	R'	m.p. (°C)	% Sn Found (Calcd.)	% C Found (Calcd.)	% H Found (Calcd.)	% Cl Found (Calcd.)
C_6H_5	C_6H_5	72.5-73.5	27.53 (27.64)	53.13 (53.84)	3.53 (3.77)	8.25 (8.52)
CH_3	CH_2Cl	126.5-128	42.86 (42.74)	17.79 (17.30)	3.13 (2.91)	25.16 (25.53)

TABLE XXIII

Summary of Attempts to Isolate $(\underline{p}\text{-XC}_6\text{H}_4\text{COO})\text{SnY}(\text{CH}_3)_2$

X	Y	Reactants ^a	Result
H	Cl	(1)	bis(benzoate) and stannoxane ^b formed
H	Cl	(2)	free acid precipitated
H	Cl	(4)	bis(benzoate) formed.
H	Br	(1)	bis(benzoate) and stannoxane formed
Cl	Cl	(1)	free acid formed
Cl	Cl	(2)	bis(benzoate) precipitated
CH ₃	Cl	(1)	product melted at 95-98°, % Sn = 35.83 vs. expected value of 37.16.
CH ₃	Cl	(3)	product melted at 258° (decomp.) % Sn = 43.23 vs. expected value of 37.16.
CH ₃ O	Cl	(1)	bis(benzoate) precipitated
CH ₃ O	Cl	(1)	free acid formed

^a (1) $(\text{CH}_3)_2\text{SnX}_2$ and $(\underline{p}\text{-XC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$

(2) $(\text{CH}_3)_2\text{SnX}_2$ and $\underline{p}\text{-XC}_6\text{H}_4\text{COOH}$

(3) $[\text{Cl}(\text{CH}_3)_2\text{Sn}]_2\text{O}$ and $\underline{p}\text{-XC}_6\text{H}_4\text{COOH}$.

(4) $(\text{CH}_3)_2\text{SnX}_2$ and $\text{R}_3\text{Sn}(\text{OOC}_6\text{H}_5)$.

^b Stannoxane = $[(\underline{p}\text{-XC}_6\text{H}_4\text{COO})\text{Sn}(\text{CH}_3)_2]_2\text{O}$.

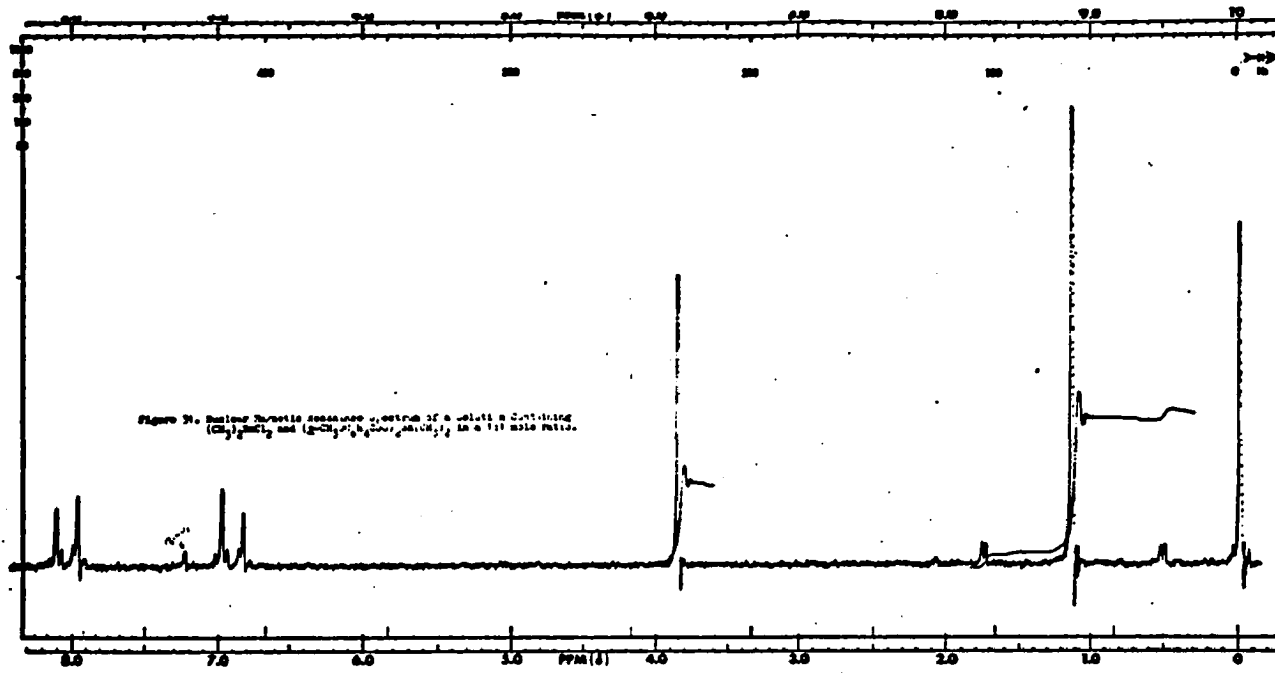
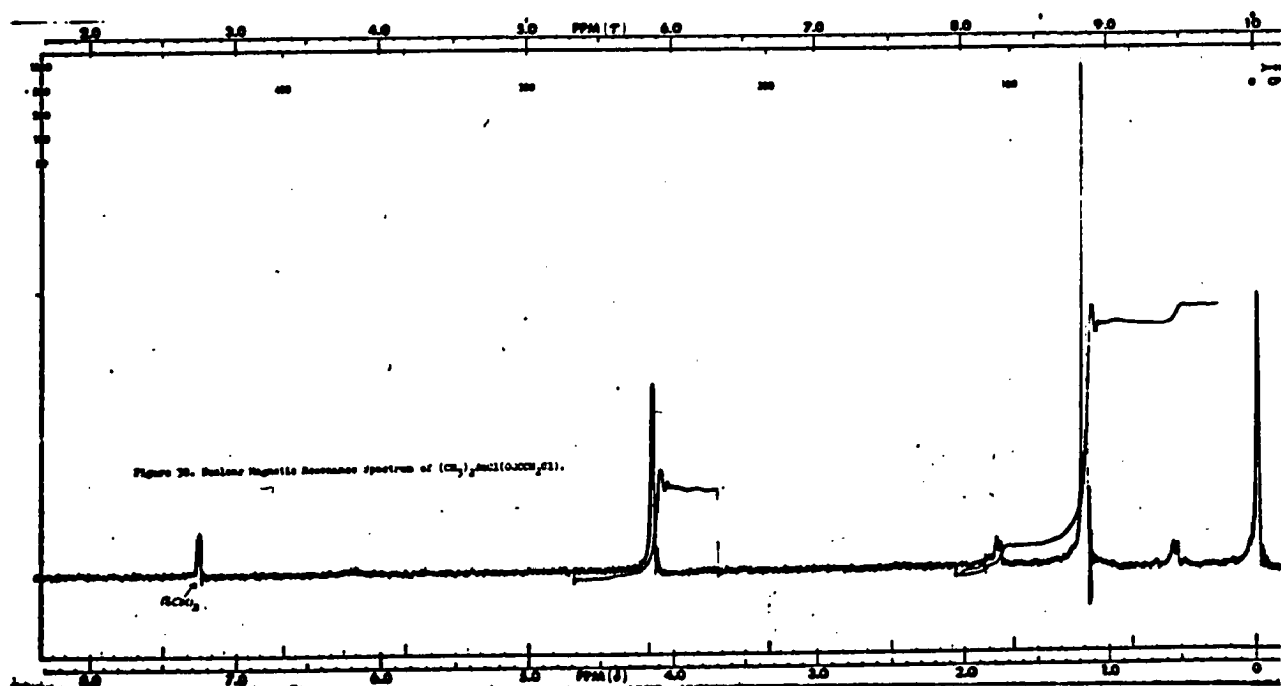


TABLE XXIV

Proton Magnetic Resonance Spectra of $(\text{CH}_3)_2\text{SnCl}(\text{OOCR})^a$

R	$J(^{117}\text{Sn}-\text{CH}_3)$ (cps)	$J(^{119}\text{Sn}-\text{CH}_3)$ (cps)	$\tau(\text{Sn}-\text{CH}_3)$ (ppm)	Reference
CH_3	72.0	76.5	8.88 (7.86) ^b	18
C_2H_5	73.5	76.8	8.87	18
CH_2Cl	71.3	74.8	8.83 (5.20) ^c	this work
$\text{p-CH}_3\text{C}_6\text{H}_4$	73.5	77.2	8.84 (7.58) ^d	this work

^aIn CDCl_3 at room temperature. ^b $\tau(\text{OOCH}_3)$; TMS = 10 ppm.

^c $\tau(\text{OOCH}_2\text{Cl})$. ^d $\tau(\text{para-CH}_3)$; ratio of $\text{p-CH}_3:\text{Sn-CH}_3 = 1:1.84$

vs. a theory of 1:2; also a small very broad peak at 6.54 ppm. This compound was not isolated; see text.

TABLE XXV

Mössbauer Parameters for $(\text{CH}_3)_2\text{SnCl}(\text{OOCR})^a$

R	ΔE	δ_o^b	Experimental Error
CH_3	3.63	1.32	± 0.007
CH_2Cl	3.84	1.42	± 0.01

^a Data at 77°K in mm/sec.

^b With respect to BaSnO_3 as source.

TABLE XXVI

COO Stretching Frequencies for $R_2SnCl(OOCR')$ ($cm.^{-1}$)						
R	R'	ASYMMETRIC		SYMMETRIC		REFERENCE
		<u>Solid</u>	<u>Soln.^a</u>	<u>Solid</u>	<u>Soln.</u>	
CH ₃	CH ₃	1564	1596	1455 (1413)	1383	18
CH ₃	CH ₂ Cl	1583	1632	1397	1371	This work
CH ₃	C ₂ H ₅	1540	1593	1465	1403	18
C ₆ H ₅	C ₆ H ₅	1547	1547	1377	1384	This work

^a In CHCl₃.

TABLE XXVII

Separation of COO Stretching Frequencies for $R_2SnX(OOCR')$

R	R'	X	Solid ^a	B ^b	Solution ^a	C ^c
CH ₃	CH ₃	Cl	130	0.96	213	1.57
CH ₃	CH ₃	Br ^d	134	0.98	217	1.60
CH ₃	CH ₃	I ^d	136	1.00	220	1.62
CH ₃	CH ₂ Cl	Cl	186	0.97	261	1.45
CH ₃	C ₂ H ₅	Cl ^d	75	0.52	193	1.33
C ₆ H ₅	C ₆ H ₅	Cl	170	0.93	163	0.89
C ₆ H ₅ ^e	C ₆ H ₅	-	141	1.01	206	1.47

^a From Table XXVI. ^b B = separation in solid/separation of NaOOCR. ^c C = separation in solution/separation of NaOOCR.

^d Reference 18. ^e For (C₆H₅)₂Sn(OOCC₆H₅)₂.

TABLE XXVIII

Sn-C and Sn-Cl Stretching Frequencies of $R_2SnCl(OOCR')$ (cm^{-1})

R	R'	Asym. Sn-C		Sym. Sn-C		Sn-Cl ^a
		<u>Solid</u>	<u>Soln.</u>	<u>Solid</u>	<u>Soln.</u>	<u>Solid</u>
CH ₃	CH ₃	578 ^b	568 ^b	528	527	326 ^c
CH ₃	CH ₂ Cl	578	565	524	523	330
C ₆ H ₅	C ₆ H ₅	d	d	d	d	317

^aNujol mull between CsBr plates. ^bReference 18.

^cThis work and reference 18. ^dLowest range of infrared instrument is 300 cm^{-1} .

CHAPTER V

DISCUSSION

A. Dimethyltin bis (carboxylates).

1) Synthesis.

The different procedures used to synthesize the dimethyltin bis (benzoates) are outlined in Chapter III. These procedures are compared in Table XXIX. Refluxing dimethyltin oxide with the respective acid, Procedure C, was seen to consistently afford a higher yield. Moreover, in this procedure it was not necessary to isolate any intermediates. In addition, as indicated by the melting point, the purity of the product obtained using Procedure C was higher.

The analytical data, given in Table XII were in agreement with theoretical values for these compounds except for $(p\text{-CNC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ which, compared to the theoretical values, was low in percent tin and percent nitrogen while high in percent carbon. However, the NMR spectrum of this compound shows the correct ratio of methyl hydrogens to phenyl hydrogens. The discrepancy in the analytical data is attributed to the presence of small traces of the reaction solvent, chlorobenzene. Chlorobenzene has a

TABLE XXIX

Comparison of Methods Used to Synthesize $(p\text{-XC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$

X	Procedure	% Yield	Comments
H	A	37	-
	B	-	intractable oil formed.
	C	70	-
Cl	A	-	distannoxane formed.
	B	43	synthesis of distannoxane required.
	C	93	-
	D	-	mainly acid or distannoxane formed.
NH ₂	A	-	distannoxane formed.
	B	61	synthesis of distannoxane required.
	C	75	washing with heptane removes last traces of solvent.
NO ₂	C	88	procedures A, B, and D not attempted.
CH ₃ O	C	81	procedures A, B, and D not attempted.
CH ₃	C	87	last traces of solvent difficult to remove.
CN	C	96	was not able to remove last traces of solvent.
CH ₃ ^a	C	80	procedures A, B, and D not attempted.
CH ₂ Cl ^b	C	77	-

^aOrtho isomer.

^bFor $(\text{CH}_3)_2\text{Sn}(\text{OOCCH}_2\text{Cl})_2$.

higher carbon content (64.5%) than the calculated value for the desired product (46.1%).

Subsequent to the preparation of diphenyltin bis (benzoate) in this investigation its preparation was reported in another laboratory.¹⁴⁶ The reported data on this compound agree with the properties given in Table XII.

2) Molecular Weights.

The molecular weights, listed in Table XIII, were determined by means of a vapor pressure osmometer. It is evident that the dimethyltin bis(p-substituted benzoates) are monomeric in very dilute solutions. If K at infinite dilution may be used at other concentrations (see Experimental, Chapter VII for details), the existence of associated species at higher concentrations is indicated.

3) NMR Spectra.

The salient features of the NMR spectra for the dimethyltin bis(carboxylates) studied are listed in Table XIV. Data for dimethyltin bis(acetate) is included for comparison. Although the donor strengths of the corresponding acids vary considerably,¹³⁷ the coupling constant, $J(^{119}\text{Sn}-\text{C}-\text{H})$, showed only a small range of values (81.5-85.5 Hz) and the chemical shift, $\tau(\text{Sn}-\text{CH}_3)$, was constant within experimental error

(8.81-8.83 ppm). If it is assumed that a relationship exists between J and percent s-character,^{14,15,27} then the Sn-C bonds of all compounds have approximately the same percent s-character. No simple relationship was found in plotting J vs. either the percent s-character or vs. σ_p .

The range of J values found for the dimethyltin bis(benzoates) corresponds to similar values (82-84 Hz) for other dimethyltin bis(carboxylates or dithiocarbamates) (see Table I). This range, intermediate between values found for dimethyltin bis(chelates) with cis (71.2 Hz) or trans (99.3 Hz) methyl groups, implied the presence of a rapid equilibrium between cis and trans configurations. However, such a possibility was discounted since no significant change in the spectra of the dimethyltin bis(benzoates) was observed at -55°C .

A more likely possibility is that the dimethyltin bis(benzoates) have internally chelating COO groups in solution with a non-linear C-Sn-C configuration (Figure 32). This would agree with the configurations proposed for either dimethyltin bis(acetate)²⁰ or dimethyltin bis(dithiocarbamate)²² in solution.

In studying the NMR spectra of dimethyltin bis(benzoate) in various solvents J was found to increase markedly in highly

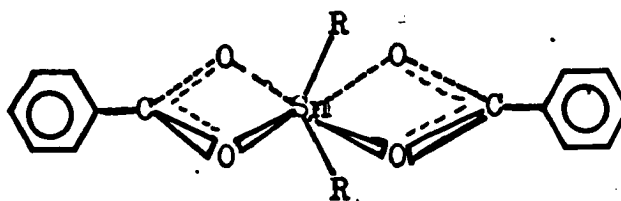


Figure 32. Proposed configuration of dimethyltin bis(benzoates) in solution with a non-linear C-Sn-C moiety.

basic solvents.¹⁴⁸ This was explained as arising from the solvent molecules replacing the weakly coordinated C-O groups, forcing the C-Sn-C moiety into a linear configuration, increasing J. Table XXX lists J values for different dimethyltin bis (p-substituted benzoates) in some basic solvents. The values of J for different compounds in the same solvent are constant. This result suggests that the nature of the solvent has a greater effect on the s-electron density of the tin atom in these compounds than the nature of the p-substituent of the benzoate group.

4) Mössbauer Spectra.

All of the dimethyltin bis(benzoates) showed a Mössbauer effect at room temperature (large recoilless fraction) and at 77°K. Although the room temperature spectra were not as intense as the spectra at 77°K, the mere existence of the effect at room temperature indicates that these compounds are polymeric in the solid state.⁴⁵ The Mössbauer parameters of these compounds at 77°K are listed in Table XV. According to the Fitzsimmons relationship,^{51,52} mentioned in Chapter I, that $\Delta E_{\text{trans}} = 2\Delta E_{\text{cis}}$, the magnitude of the quadrupole splittings at 77°K corresponds to a trans configuration for the C-Sn-C moiety.

In Figures 33 and 34, respectively, the Mössbauer chemical shifts, δ_o , and quadrupole splittings, ΔE , at 77°K

TABLE XXX

NMR Spectra of $(\underline{p}\text{-XC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ in Basic Solvents.

X	Solvent	$J(^{119}\text{Sn-C-H})$ (Hz)
H	DMSO	104.5 (105.4) ^a
NO ₂	DMSO	104.2
Cl	DMSO	104.2
NH ₂	DMSO	104.4
NH ₂	Acetone	90.0 (90.5) ^a

^aRef. 148.

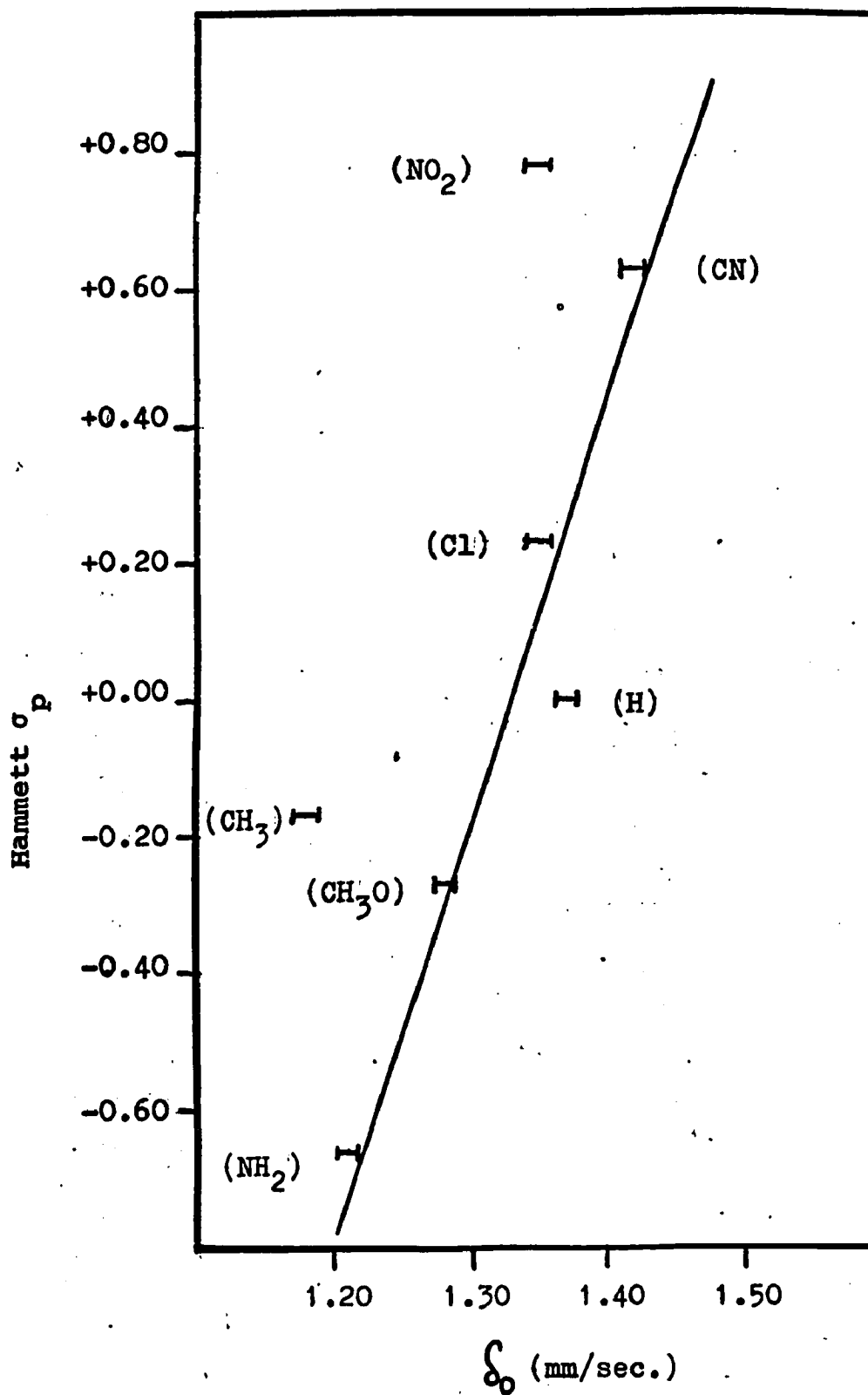


Figure 33. Variation of Mössbauer chemical shift, δ_0 , with Hammett σ_p .

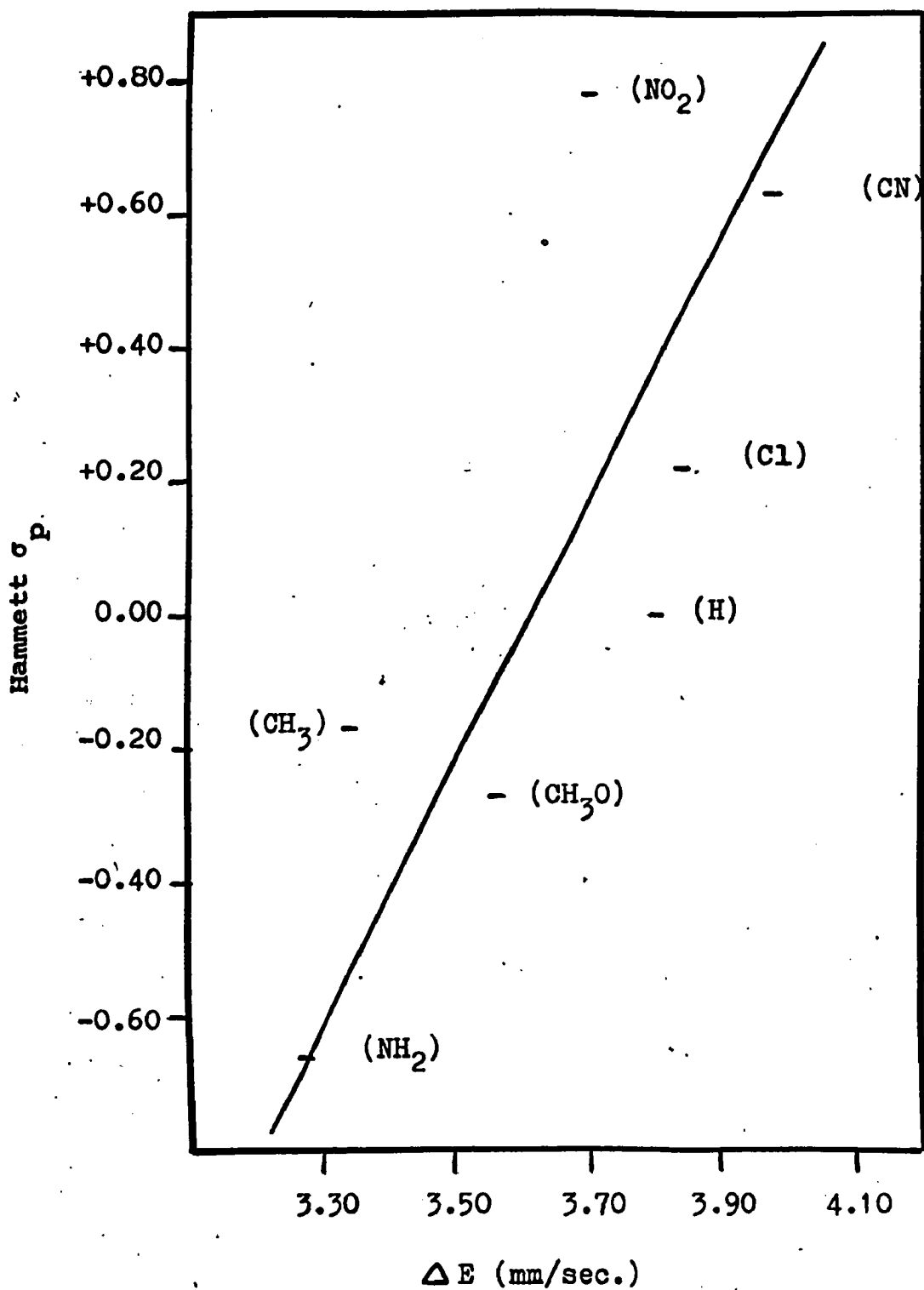


Figure 34. Variation of Mössbauer quadrupole splitting, ΔE , with Hammett σ_p .

are compared with the Hammett σ_p constants.¹³⁷ In contrast to the NMR data the Mössbauer parameters vary markedly with different acids. The existence of a rough linear relationship between δ_o and σ_p was taken as evidence for the variation of the polarity of the tin-oxygen bonds with a change in donor strength of the carboxylates in the present series of dimethyltin bis(benzoates).

Inspection of Figure 33 shows that, in going from electron donating to electron withdrawing groups, the Mössbauer chemical shift, δ_o increases. We view the effect of electron withdrawing groups as registered predominantly at the carboxyl group, whose electron density lowers the effective s-electron density at tin by shielding. Electron withdrawing groups in the para-position of the benzene ring weaken the donor power of the carboxyl group, causing δ_o to increase in the direction associated with Sn(II).^{148a} A similar explanation was proposed by Zuckerman and co-workers in studying a homologous series of halosubstituted tri-alkyltin acetates.¹⁸¹

5) Infrared Spectroscopy.

Sn-C Region: Table XVI lists the infrared active bands attributed to the asymmetric and symmetric tin-carbon stretching vibrations for the dimethyltin bis(benzoates)

studied. All of the compounds have two such bands in the range of $500\text{--}600\text{ cm}^{-1}$. This indicates that the dimethyltin bis(benzoates) have a non-linear C-Sn-C moiety, similar to that proposed for dimethyltin bis(acetate),²⁰ dimethyltin bis(N,N-dimethyldithiocarbamate)²², and dimethyltin bis(kojate).¹⁴⁹

The high values of the asymmetric stretching frequencies ($570\text{--}589\text{ cm}^{-1}$) are not limited to dimethyltin bis(benzoates). Other dimethyltin bis(chelates) have a similar range ($570\text{--}578\text{ cm}^{-1}$);^{17,20} and they are considered to contain six-coordinate tin atoms with non-linear methyl groups. The dimethyltin bis(p-substituted benzoates) have a similar structure.

COO Region: The positions of the asymmetric and symmetric COO stretching frequencies of the dimethyltin bis(carboxylates) are listed in Table XVIII. Assignments were made by comparison with the infrared spectra of the respective sodium carboxylates (see Table XVII and Appendixes 12-22). In order to ascertain whether the mode of bonding of the carboxyl group may be inferred from infrared spectroscopy, comparison of the separation, Δ , ($\Delta = \nu_{\text{asym.}} - \nu_{\text{sym.}}$) of the dimethyltin bis(carboxylates) and the analogous separation of the respective sodium carboxylates is made in Table XXXI. The ratios between the separations in the solid dimethyltin bis(carboxylates) and the separations of the respective sodium carboxylates are listed in the fourth column and designated

TABLE XXXI

Separation of COO Stretching Frequencies of $(\text{CH}_3)_2\text{Sn}(\text{OOCR})_2$ (cm.^{-1})					
R	NaOOCR ^a	Solid ^b	B ^c	Solution ^b	C ^d
C_6H_5	140	183	1.31	210	1.50
$\text{p-CH}_3\text{OC}_6\text{H}_4$	129	172	1.33	208	1.61
$\text{p-NH}_2\text{C}_6\text{H}_4$	141	185	1.31	Insoluble	-
$\text{p-NO}_2\text{C}_6\text{H}_4$	182	220	1.21	Insoluble	-
$\text{p-CNC}_6\text{H}_4$	149	157	1.05	206	1.38
$\text{p-ClC}_6\text{H}_4$	143	172	1.20	206	1.44
$\text{p-CH}_3\text{C}_6\text{H}_4$	134	146	1.09	207	1.55
CH_3	136	174	1.28	200	1.47
ClCH_2	180	219	1.22	272	1.51
C_2H_5	145	186	1.28	203	1.40

^a From Table XVII. ^b From Table XVIII; average values are used when more than one band is listed. ^c B = separation in solid/separation of NaOOCR. ^d C = separation in solution/separation of NaOOCR.

"B" (for bridging). The ratios between the separations of the dimethyltin bis(carboxylates) in solution and the separations of the respective sodium carboxylates are listed in the sixth column and designated "C" (for chelating). Column B is seen to have a range of 1.05-1.33 while column C has a range of 1.38-1.61.

It has already been pointed out that the molecular weight studies at the higher concentrations in solution and Mössbauer effect studies in the solid at room temperature are consistent with a polymeric structure for the dimethyltin bis(benzoates). It is suggested that the "B" ratio range corresponds to the carboxyl group bridging two different tin atoms as in Figure 1-d. On the other hand, NMR (similar values of J and τ) and molecular weight data of these same compounds indicate a monomeric structure in dilute solutions. It is suggested that the "C" ratio range corresponds to an internally chelating carboxyl group as in Figure 1-c.

The data in Table XXXII support the assumption that the range of the "B" ratios correspond to a bridging carboxyl group. The separation of the COO stretching frequencies for trialkyltin carboxylates are tabulated in this table along with the respective "B" ratios. The range of 0.94-1.32 is similar to the "B" ratios for dimethyltin bis(carboxylates).

TABLE XXXII

Separation of COO Stretching Frequencies
of $R_3\text{SnOOCR}'$ (cm.^{-1})

R	R'	NaOOCR' ^a	Solid	B
CH ₃	CH ₃	136	153 ^b	1.13
CH ₃	ClCH ₂	180	237 ^c	1.32
CH ₃	Cl ₂ CH	241	240 ^c	1.00
CH ₃	Cl ₃ C	320	300 ^c	0.94
CH ₃	C ₁₁ H ₂₃	145	157 ^b	1.08
CH ₃	H	222	240 ^d	1.08
C ₂ H ₅	H	222	236 ^e	1.06
C ₂ H ₅	CH ₃	136	180 ^e	1.32
C ₂ H ₅	C ₆ H ₅	140	180 ^e	1.29
n-C ₄ H ₉	CH ₃	136	162 ^b	1.19
n-C ₄ H ₉	ClCH ₂	180	192 ^f	1.07
n-C ₄ H ₉	Cl ₂ CH	241	263 ^f	1.09
n-C ₄ H ₉	Cl ₃ C	320	306 ^f	0.96
n-C ₆ H ₁₃	CH ₃	136	162 ^b	1.19

^aFrom Table XVII. ^bReference 7. ^cReference 150.

^dReference 151. ^eReference 81. ^fReference 126.

Recent x-ray studies have shown that trialkyl-¹⁵² and triaryltin⁶³ carboxylates are polymeric with bridging carboxyl groups.

In studying alkali metal benzoates Green, Kynaston, and Lindsey¹⁵³ noted an increase in Δ in going from lithium to cesium. However, no simple linear relationship was found (a) when Δ was plotted against the polarizability values of the free ions;¹⁵⁴ (b) when Δ was plotted against the electronegativity values of the alkali metals;¹⁵⁵ (c) when the symmetric COO stretching frequency was plotted against the electronegativity values of the alkali metals.¹⁵³

For the present investigation no simple relationships were found in any of the following: (a) J vs. either the percent s-character or σ_p ; (b) δ_o vs. either the asymmetric or symmetric COO stretching vibrations; (c) ΔE vs. either the asymmetric or symmetric COO stretching vibrations; (d) ΔE vs. either Δ_{solid} or $\Delta_{\text{soln.}}$ of the COO stretching vibrations; (e) Δ_{solid} vs. the pK_a ; (f) $\Delta_{\text{soln.}}$ vs. the pK_a ; (g) $\Delta_{\text{soln.}}$ vs. either the asymmetric or symmetric COO stretching vibrations; (h) pK_a vs. the values of the "B" range.

However, a linear relationship was shown (Figure 35) to exist between the pK_a of the respective benzoic acid and the corresponding "C" ratio. In addition, a linear relationship was found (Figure 36) between Δ_{solid} and the symmetric

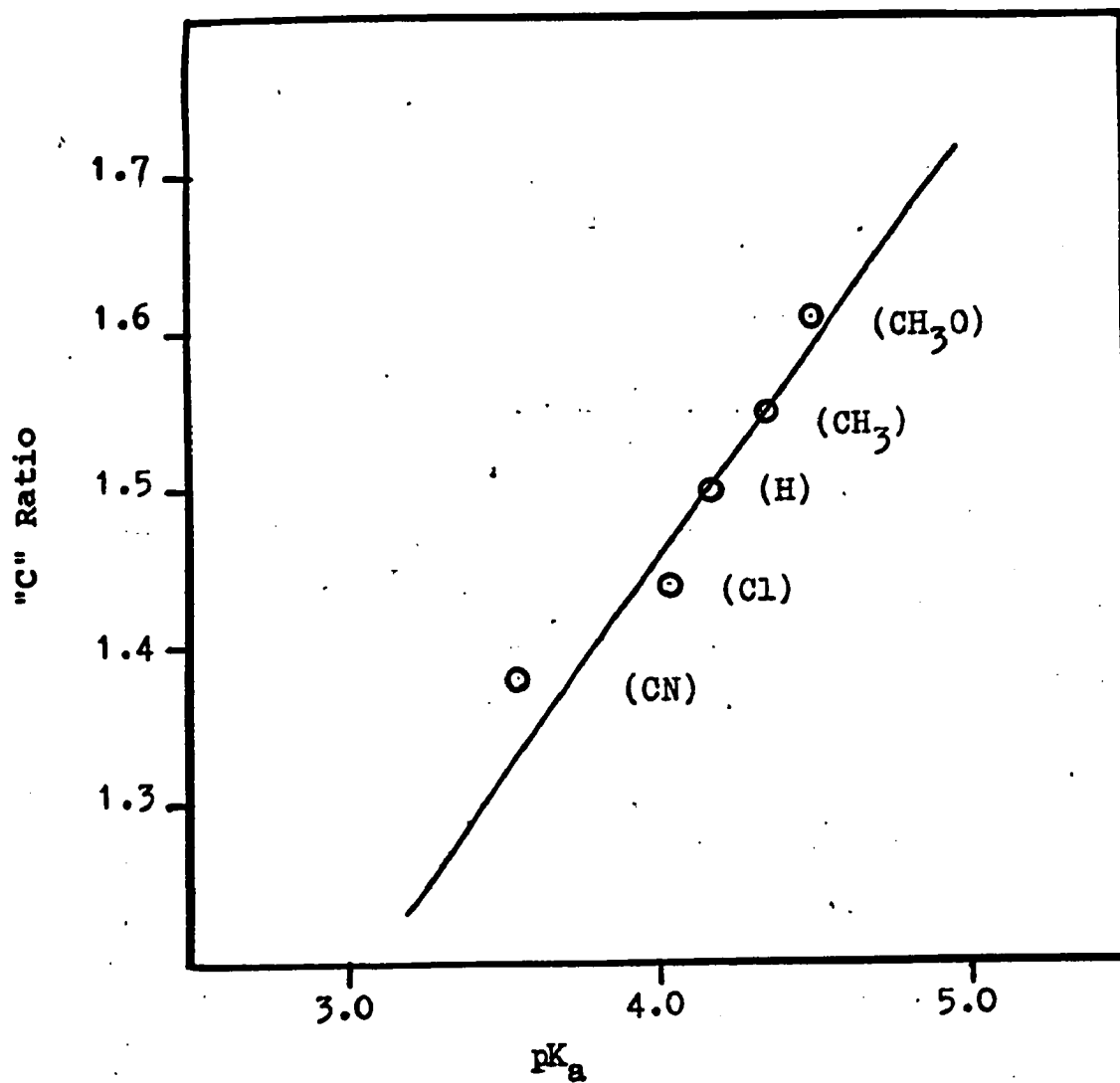


Figure 35. Variation of "C" ratio with pK_a for dimethyltin bis (benzoates).

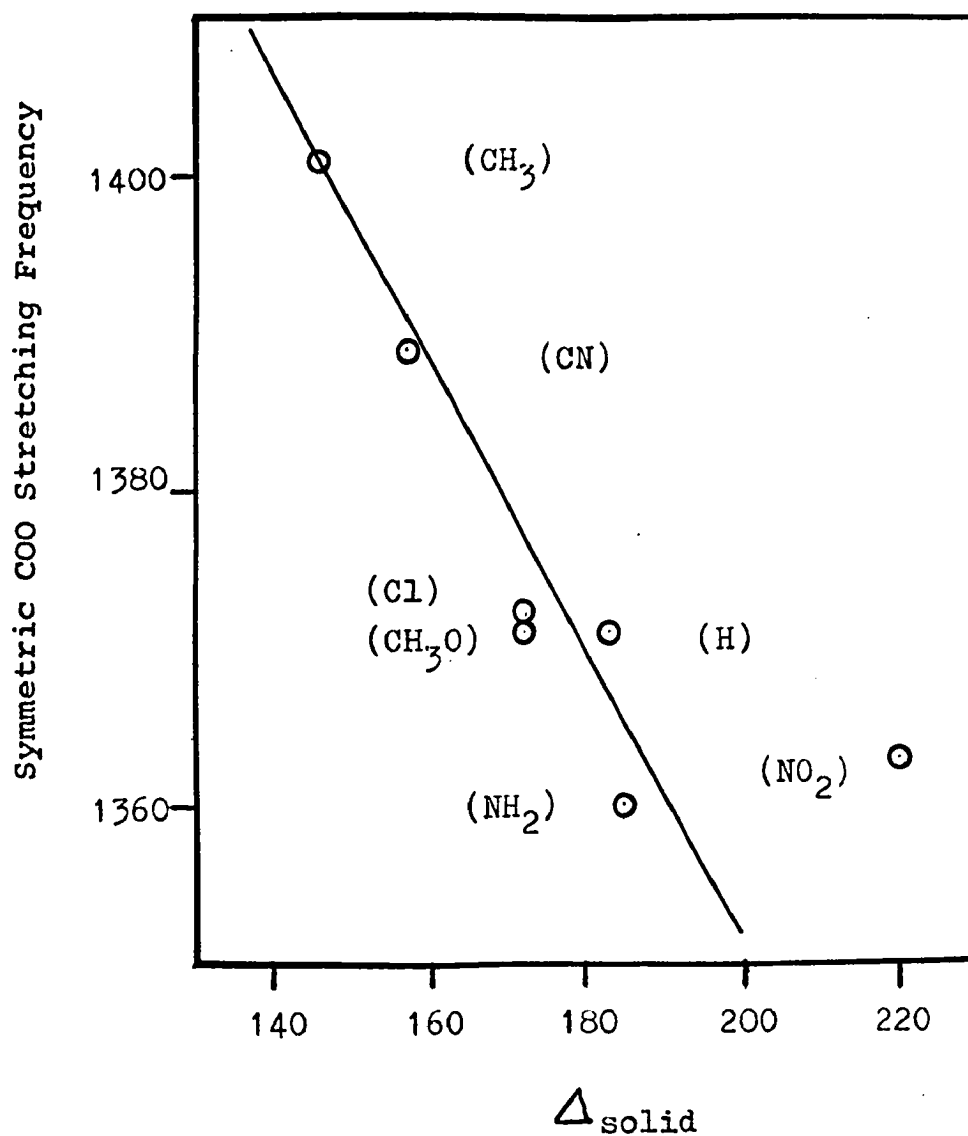


Figure 36. Variation of Δ_{solid} with the respective symmetric COO stretching frequency, for dimethyltin bis(benzoates).

COO stretching frequencies. The former relationship may be understood since the separation, Δ , in solution is almost constant ($206-210 \text{ cm}^{-1}$) while the separation of the corresponding sodium carboxylates vary with the para-substituent. An explanation for the linear relationship between Δ_{solid} and the COO symmetric stretching vibration depends upon understanding why there is a variation in Δ .

The effect of the rigidity of the COO group is seen in the changes in $\nu_{\text{asym.}}$ and $\nu_{\text{sym.}}$ (COO). An increase in rigidity should give rise to an increase in frequency in going from the sodium salt (COO group not bonded to other atoms, as in Figure 1-a) to solid (COO group part of, at least, an eight-membered ring, as in Figure 1-d) to solution (COO group constrained to a four-membered ring, as in Figure 1-c). On the other hand, the effect of increasing the mass of the molecule will contribute to a decrease in the magnitudes of $\nu_{\text{asym.}}$ and $\nu_{\text{sym.}}$ in the order Na-carboxylate > solution > solid.

Table XXXIII summarizes the COO stretching frequencies for the dimethyltin bis(carboxylates) and the respective sodium carboxylates. Inspection shows that for most compounds the asymmetric band increases in the order Na-carboxylate < solid < solution, while the opposite is generally true for the symmetric band. Apparently the rigidity of the COO group predominates in determining changes in $\nu_{\text{asym.}}$ (COO) while both the

TABLE XXXIII

COO Stretching Frequencies of $(\text{CH}_3)_2\text{Sn}(\text{OOCR})_2$

and of NaOOCR^a (cm.^{-1})

R	Asymmetric			Symmetric		
	<u>Na^b</u>	<u>Solid</u>	<u>Solution</u>	<u>Na</u>	<u>Solid</u>	<u>Solution</u>
C_6H_5	1547	1554	1568	1407	1371	1358
$\text{p-CH}_3\text{OC}_6\text{H}_4$	1530	1544	1559	1401	1371	1351
$\text{p-NH}_2\text{C}_6\text{H}_4$	1532	1545	-	1391	1360	-
$\text{p-NO}_2\text{C}_6\text{H}_4$	1584	1583	-	1402	1363	-
$\text{p-CNC}_6\text{H}_4$	1548	1546	1552	1399	1389	1346
$\text{p-ClC}_6\text{H}_4$	1537	1544	1555	1394	1372	1349
$\text{p-CH}_3\text{C}_6\text{H}_4$	1550	1547	1558	1416	1401	1351
CH_3	1576	1580	1607	1440	1406	1407
ClCH_2	1598	1611	1633	1418	1392	1361
C_2H_5	1560	1585	1607	1415	1399	1402

^aData from Tables XVII and XVIII; average values are used when more than one band is listed. ^b NaOOCR .

rigidity of the COO group and the mass effect predominate in determining changes in $\nu_{\text{sym.}}(\text{COO})$. The overall effect is that the separation between these two bands steadily increases in the order Na-carboxylate < solid < solution.

This approach explains the increase in Δ in going from sodium salt to solution. In addition, it is apparent that the mass effect influences $\nu_{\text{sym.}}(\text{COO})$ in such a way that Δ_{solid} varies directly with it. However, it should be noted that these correlations are dependent upon the proposed structures of the dimethyltin bis(benzoates) in both the solid and solution.

Sn-O Region: The tin-oxygen stretch for the dimethyltin bis(benzoates) are listed in Table XIX. However, no relationship was found between the assigned bands and the donor properties (e.g., σ_p) of the carboxylates. Because of the numerous weak bands present in the region of interest ($300\text{--}450\text{ cm}^{-1}$) these assignments are to be considered tentative.

6) Conclusions.

The present study indicates that the dimethyltin bis(benzoates) studied are polymeric in the solid state with bridging carboxyl groups. In dilute solutions these compounds are monomeric with internally chelating carboxyl groups. To

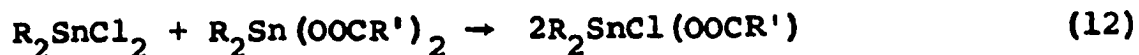
retain the six-coordinate nature of tin these structures require that tin be part of at least, an eight-membered ring in the solid state and part of a four-membered ring in solution. In addition, the dimethyltin bis(benzoates) have a non-linear C-Sn-C moiety in both the solid state as well as in solution.

The bonding properties of these compounds were found to vary between solid and solution. In the solid state the polarity of the tin-oxygen bonds varies with the donor strength of the carboxylate. In solution, however, the percent s-character of the Sn-C bonds is essentially constant. The present investigation also suggests that the mode of bonding of a carboxyl group in a non-transition metal carboxylate may be determined by comparison of the infrared spectrum of the compound with the infrared spectrum of the corresponding sodium carboxylate.

B. Exchange Reactions.

1) Introduction

One of the objectives of this investigation was to prepare a series of dimethyltin halide benzoates. However, all attempts to synthesize these compounds (vide infra) were unsuccessful. In particular, attempts according to Equation 12,



($R = CH_3$; $R' = \underline{p}$ -substituted benzoate) varying the relative concentrations of the reactants, yielded a solution with a tin-methyl coupling constant, J , equal to the weighted average of the J values of the reactants. Figure 27 shows the regular increase in J upon increasing the concentration of dimethyltin bis($\underline{p}$ -methoxybenzoate) relative to the concentration of dimethyltin dichloride. At all concentrations only a single peak attributable to the $Sn-CH_3$ groups was detectable. However, J is seen to be proportional to the mole ratio of the reactants. For example, when the reactants are present in a 1:1 mole ratio, J is found to be 76.8 Hz - the average of the reactants (68.9 Hz for dimethyltin dichloride and 83.8 Hz for dimethyltin bis ($\underline{p}$ -methoxybenzoate)). This averaging of coupling constants is attributed to rapid intermolecular exchange of ligands between the different dimethyltin species present.⁸⁹ Methyl groups on tin are known to labilize the other ligands.⁹¹

The methyl region of the NMR spectra of some methyltin chlorides and methyltin benzoates is shown, schematically, in Figure 37. Each spectrum consists of a large singlet overlaid by a pair of small flanking doublets, from which $J(^{119}Sn-C-H)$ may be determined. In Figure 37 only the outer set of side bands is shown. It is evident that NMR spectra

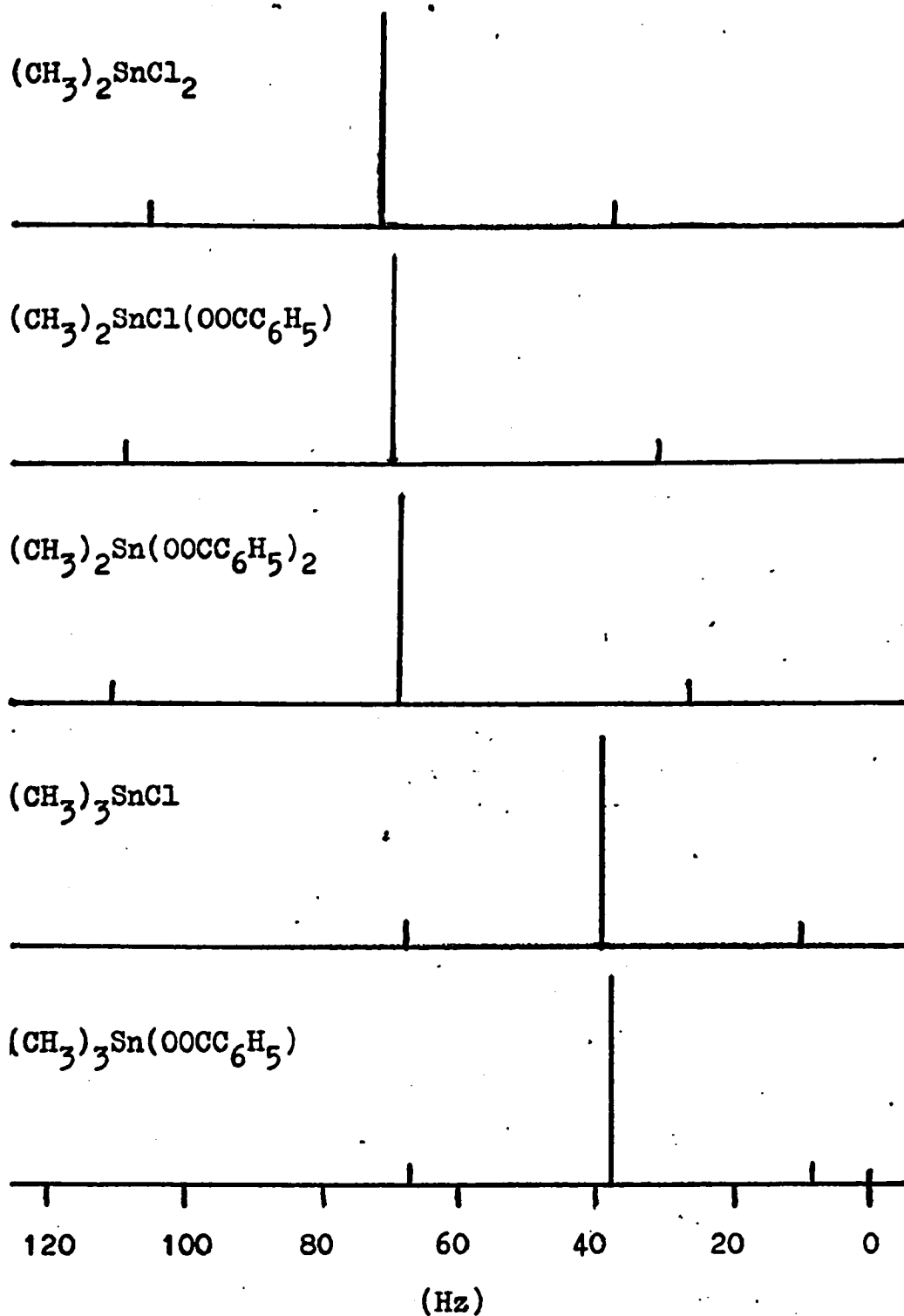
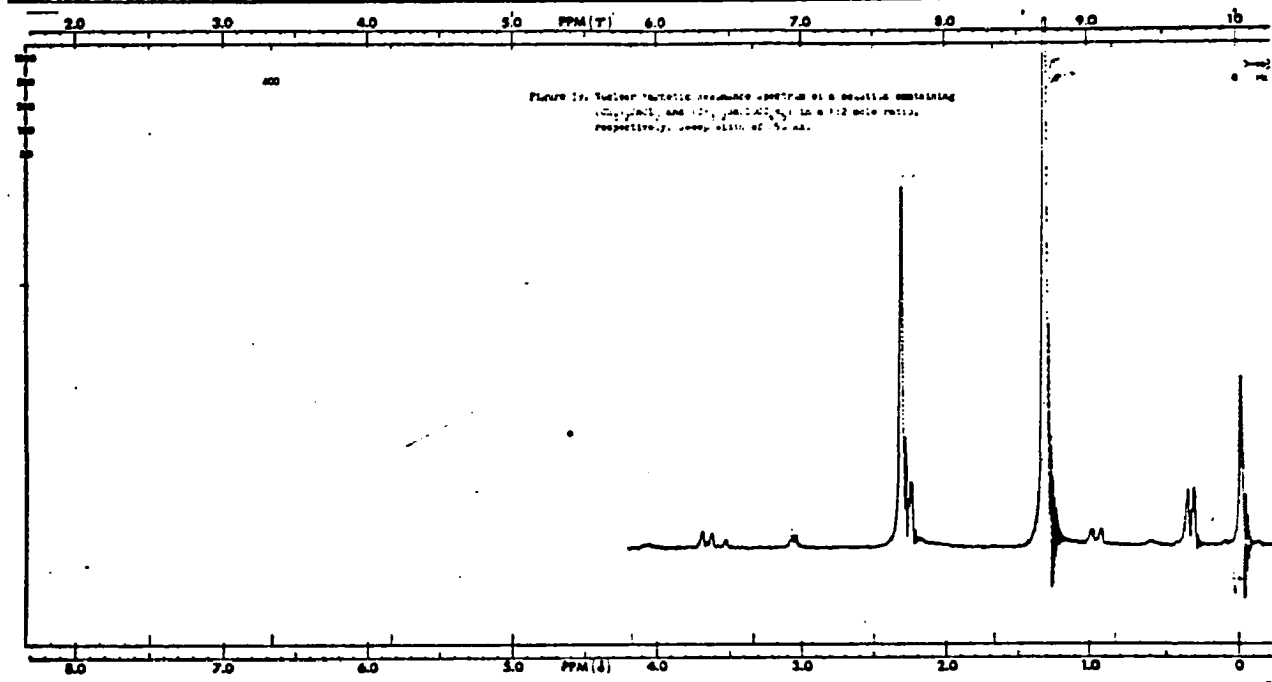
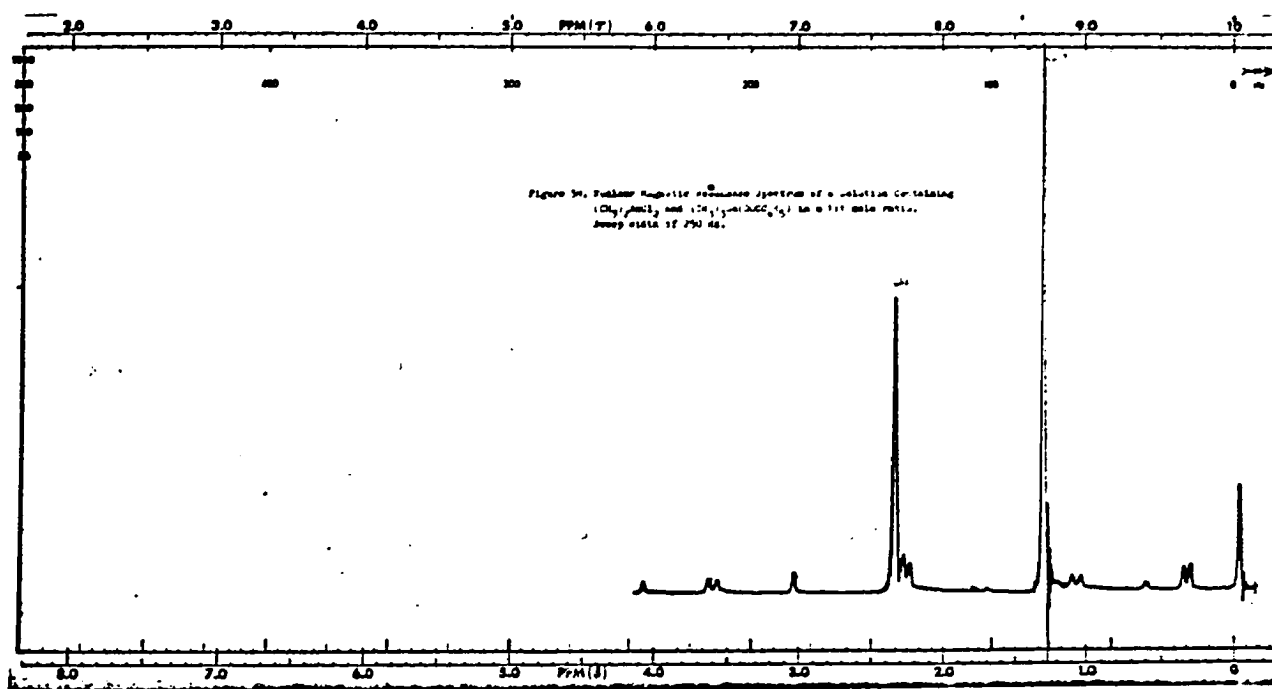


Figure 37. Schematic NMR spectra of some methyltin chlorides and methyltin benzoates.

can be used to distinguish between trimethyltin and dimethyltin species. In addition, the individual dimethyltin species are distinguishable by their different J values. Hence, assuming no interactions, NMR spectroscopy can be used to determine the presence of each species in solution.

The results of a study of various mixtures of methyltin chlorides and methyltin benzoates are tabulated in Table XX. The spectrum of a mixture of dimethyltin dichloride and trimethyltin chloride in a 1:1 mole ratio showed no interaction. On the other hand, the spectrum of a solution of $(\text{CH}_3)_2\text{SnCl}_2$ and $(\text{CH}_3)_3\text{Sn}(\text{OOC}_6\text{H}_5)$ in a 1:1 mole ratio showed a marked shift of τ and J (for the SnCl_2 species) to values corresponding to five-coordinate tin.^{18,19,22,23} When the mole ratio of reactants was increased to 1:2, respectively, there was a further shift in τ to 8.86 ppm and J to 82.9 Hz, corresponding to six-coordinate organotin chelates.^{20,22} Figures 38 and 39 show the NMR spectra of solutions containing dimethyltin dichloride and trimethyltin benzoate in 1:1 and 1:2 mole ratios, respectively.

The exact dependence of J for the dimethyltin species on the relative concentrations of the reactants was tested by studying the change in J over a large range of mole ratios. Figure 28 shows J as a function of the mole ratio for the

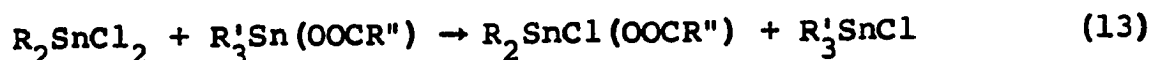


$(\text{CH}_3)_3\text{Sn}(\text{OOC}_6\text{H}_5) / (\text{CH}_3)_2\text{SnCl}_2$ system. Figure 29 shows a similar relationship for the $(\text{CH}_3)_3\text{Sn}(\text{OOCCH}_2\text{Cl}) / (\text{CH}_3)_2\text{SnCl}_2$ system. In both cases (a) J increase with increasing concentration of trimethyltin carboxylate; (b) for a 1:1 mole ratio J corresponds to values assigned for compounds of the type $(\text{CH}_3)_2\text{SnCl}(\text{OOCR})$; (c) for a mole ratio of 1:2 or greater, J approaches values corresponding to $(\text{CH}_3)_2\text{Sn}(\text{OOCR})_2$.

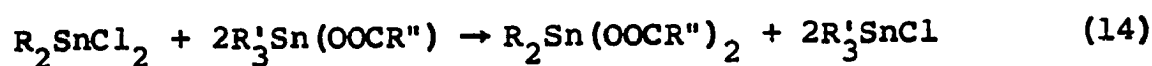
2) Scope of the Reactions

These results indicate that the reaction of triorganotin carboxylates with diorganotin dihalides depends upon the mole ratio of reactants as shown in the following equations:

1:1 mole ratio



1:2 mole ratio



Both the 1:1 and 1:2 mole ratio reactions were essentially complete within seconds after mixing, as shown by NMR spectroscopy. This is the first report of a halide for carboxylate exchange between a diorganotin and a triorganotin species. However, these reactions are not mere scrambling

of halide and carboxyl ligands between two organotin species; because addition of a large excess of $R_3'SnCl$ to either $R_2'SnCl(OOCR'')$ or to $R_2'Sn(OOCR'')_2$ does not give evidence for any reaction.

Large scale reactions were run and the products predicted from Equations 13 and 14 including trimethyltin chloride in some cases, were isolated. The various systems studied and the compounds obtained are listed in Table XXI. All products were identified by their melting points, infrared and NMR spectra and in the case of new compounds, by their elemental analysis.

Several new compounds have been synthesized by these methods. The analytical data of these compounds are shown in Table XXII. Recently, one of these compounds, diphenyltin bis(benzoate), was reported by Reichle¹⁴⁶ of Union Carbide Research Laboratories, Bound Brook, New Jersey. The data from the two laboratories are in good agreement. Analytically pure samples of both $(C_6H_5)_2SnCl(OOCC_6H_5)$ and $(C_6H_5)_2Sn(OOCC_6H_5)_2$ were obtained only from reactions and recrystallizations run at the lowest feasible temperature. A similar thermal instability was found for diphenyltin bis(acetate).¹⁵⁶

The existence of dimethyltin chloride benzoate in solution is indicated by its NMR spectra (Figure 38).

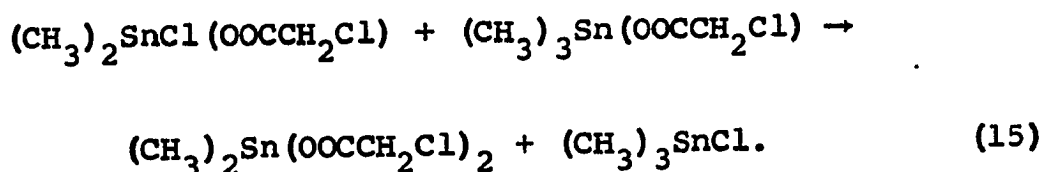
Yet, attempts to isolate $(\text{CH}_3)_2\text{SnCl}(\text{OOC}_6\text{H}_5)$ by reacting dimethyltin dichloride with either $(\text{CH}_3)_3\text{Sn}(\text{OOC}_6\text{H}_5)$ or $(n\text{-C}_4\text{H}_9)_3\text{Sn}(\text{OOC}_6\text{H}_5)$ were unsuccessful. Solutions with a mole ratio of 1:1 only afforded impure dimethyltin bis(benzoate). Similar results are obtained in the reaction of dimethyltin dichloride with dimethyltin bis(benzoate) (vide infra).

3) Proposed Mechanism

In order to propose a mechanism for the reaction system represented by Equations 13 and 14 the following three points must be kept in mind:

(a) Triorganotin carboxylates are known to contain four-coordinate tin in dilute solution with a free carbonyl group.^{7,126,127}

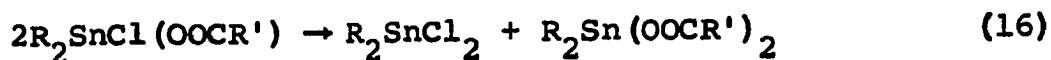
(b) The dimethyltin chloride carboxylates were found to react with an additional mole of triorganotin carboxylate to yield dimethyltin bis(carboxylates), as shown in Equation 15,



(c) Reaction of dimethyltin dichloride with triphenyltin acetate in a 1:2 mole ratio yielded impure dimethyltin bis(acetate). However, a small amount of dimethyltin chloride acetate was also isolated.

These three points suggest that with a 1:2 mole ratio (Equation 14) the reaction proceeds in a stepwise manner via a diorganotin chloride carboxylate. It is probable that the free carbonyl group of the triorganotin carboxylate initially attacks R_2SnCl_2 forming an intermediate shown in Figure 40-a with expansion of the coordination of both tin atoms to five. Breaking of the R'_3Sn-O and R_2XSn-X bonds enables $R_2SnCl(OOCR'')$ and R'_3SnCl to form. The diorganotin chloride carboxylate formed then reacts with an additional mole of triorganotin carboxylate as shown in Figure 40-b.

An alternate mechanism for these reactions is related to the structure of diorganotin halide carboxylates in solution. It has been observed^{18,157} that these compounds undergo disproportionation in solution according to Equation 16,



This suggests that, for the present series of exchange reactions, the predominate species in solution would be diorganotin dichloride and diorganotin bis(carboxylate).

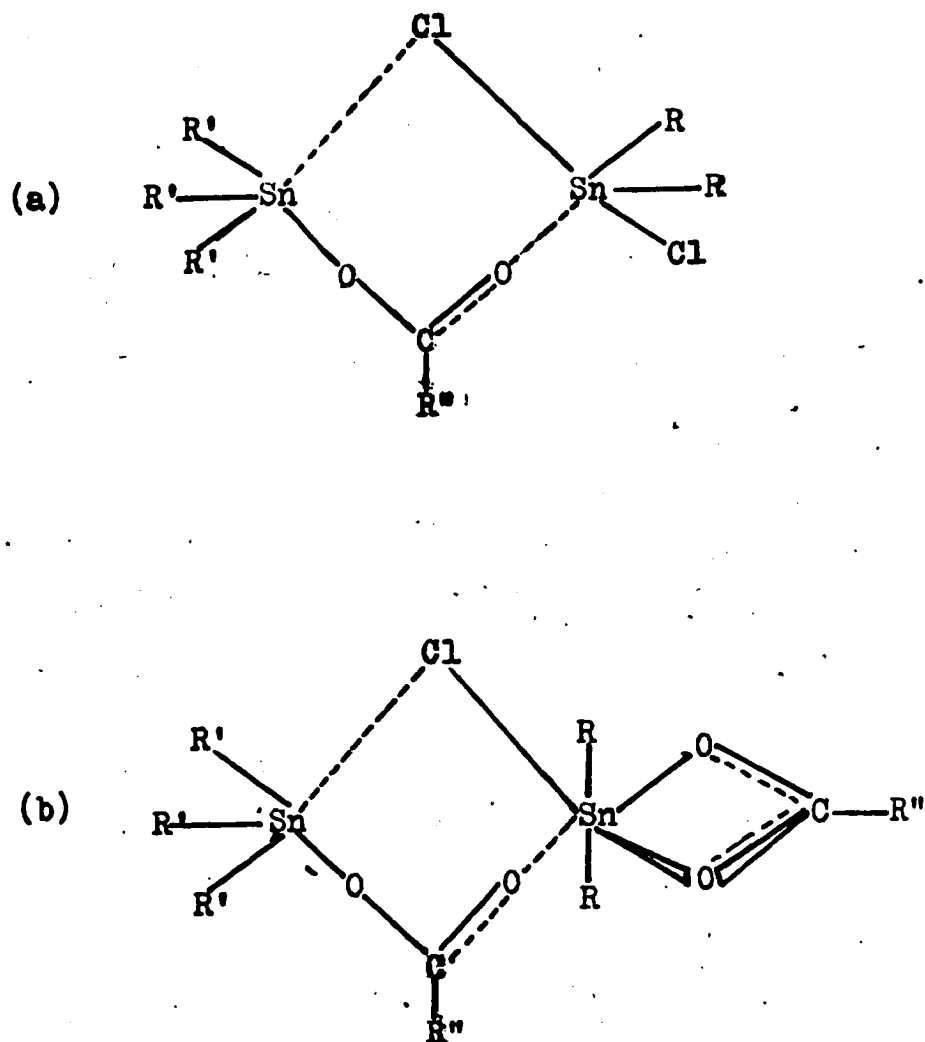


Figure 40. Proposed intermediates between (a) R_2SnCl_2 and $R'_3Sn(OOCR'')$; (b) $R_2SnCl(OOCR'')$ and $R'_3Sn(OOCR'')$.

Rapid intermolecular exchange of carboxyl groups would explain finding only a single $(\text{CH}_3)_2\text{Sn}$ peak in the NMR spectra. Attempts at isolation would then precipitate the most stable (insoluble) compound.

This latter mechanism assumes that Equations 13 and 14 are equilibrium reactions. Evidence in favor of an equilibrium is indicated by the data of Figures 28 and 29 which show J to be below the values for the pure dimethyltin bis(carboxylates) when the mole ratios of R_2SnCl_2 and $\text{R}'_3\text{Sn}(\text{OOCR}'')$ are 1:2 or greater. However, as already pointed out, attempts at reversing Equations 13 and 14 were unsuccessful. For example, reaction of dimethyltin bis(monochloroacetate) with a threefold excess of trimethyltin chloride did not result in any reaction. The presence of any dimethyltin dichloride would cause $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$ to immediately precipitate since the reverse of Equation 16 has also been used to synthesize dimethyltin chloride monochloroacetate (vide infra). These reactions, at least for the monochloroacetate system, do not appear to be reversible.

An attempt was made to differentiate between a mechanism where the diorganotin chloride carboxylate exists in solution and a mechanism where diorganotin dichloride

and diorganotin bis(carboxylates) predominate. The coupling constant, J , for the latter mechanism should involve a simple averaging of coupling constants as given in Equation 17,

$$J_{\text{calc.}} = P_1 J_1 + P_2 J_2 + \dots P_n J_n \quad (17)$$

where $J_{\text{calc.}}$ = calculated coupling constant

J_n = coupling constant of the n th species

P_n = mole fraction of the n th species.

Table XXXIV compares the experimental coupling constant J , with that calculated for the two different mechanisms for the monochloroacetate system. Inspection shows that both approaches agree with each other within experimental error.

C. Diorganotin Halide Carboxylates.

1) Synthesis

Dimethyltin chloride monochloroacetate and diphenyltin chloride benzoate were the only diorganotin halide carboxylates isolated in pure form. Analytical data is listed in Table XXII. Seventeen separate attempts were made to isolate $(p\text{-XC}_6\text{H}_4\text{COO})\text{SnY}(\text{CH}_3)_2$ ($X = \text{H}, \text{Cl}, \text{CH}_3$, or CH_3O ; $Y = \text{Cl}$ or Br). These attempts, using various different reactions, are summarized in Table XXIII. It can be seen

TABLE XXXIV

Predicted and Experimental Coupling Constants
for Exchange Reactions^a

<u>Moles $(\text{CH}_3)_3\text{Sn}(\text{OOCCH}_2\text{Cl})$</u>	$J_{\text{calc.}}(\text{A})^b$	$J_{\text{calc.}}(\text{B})^c$	$J_{\text{experi-}}$
<u>Moles $(\text{CH}_3)_2\text{SnCl}_2$</u>			<u>mental</u>
0.50	71.9	72.1	71.3
1.00	74.8	75.2	73.9
1.50	78.2	78.4	76.6
2.00	81.5	81.5	78.5
3.00	81.5	81.5	80.3
4.00	81.5	81.5	81.2

^aIn CDCl_3 ; J values in Hz. ^bAssumes that diorganotin halide
carboxylate preferentially formed. ^cAssumes complete
disproportionation.

that most reactions result in the respective diorganotin bis(benzoate) precipitating--even though there is evidence for reaction or fast intermolecular exchange (a single Sn-CH_3 peak with J and τ values intermediate between the reactants in most cases) in solution. This lends support to the equilibrium postulated to exist between dimethyltin dihalides and dimethyltin bis(acetates) on the one hand and dimethyltin halide acetates on the other hand,^{18,157} as in Equation 16.

The only promising result was for dimethyltin chloride p-toluate. Only a very small amount of a sharp melting compound was obtained and its analysis for tin was low. Attempts to repeat these experiments on a larger scale were unsuccessful. It should be noted that changing R in $(\text{CH}_3)_2\text{SnX}(\text{OOCR})$ from alkyl to aryl can not be the sole cause of the instability of dimethyltin halide benzoates because $(\text{C}_6\text{H}_5)_2\text{SnCl}(\text{OOC}\text{C}_6\text{H}_5)$ has been synthesized in the present work. The major factor leading to the observed result is the greater stability (or insolubility) of the dimethyltin bis(benzoates) compared to the dimethyltin halide benzoates.

2) NMR Spectra

The NMR spectrum of $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$ is shown in Figure 30. Figure 31 shows the NMR spectrum of a solution containing $(\text{CH}_3)_2\text{SnCl}_2$ and $(\text{p-CH}_3\text{OC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ in a 1:1 mole ratio. Table XXIV lists the pertinent NMR data of these and other dimethyltin chloride carboxylates. Comparison with the NMR data for the related dimethyltin bis(carboxylates) (Table XIV) shows a shift in J from about 84 Hz to about 75 Hz in going from $(\text{CH}_3)_2\text{Sn}(\text{OOCR})_2$ to $(\text{CH}_3)_2\text{SnCl}(\text{OOCR})$. Comparison of the NMR data for Figure 31 and similar data for a solution containing dimethyltin dichloride and trimethyltin benzoate in a 1:1 mole ratio (Figure 38 and Table XX) shows close agreement. This lends support to the assumption that $(\text{CH}_3)_2\text{SnCl}(\text{OOC}_6\text{H}_5)$ exists in solution.

3) Mössbauer Spectra

A basic question to be considered is whether the molecule $\text{R}_2\text{SnCl}(\text{OOCR}')$ actually exists or whether it is a crystalline mixture of R_2SnCl_2 and $\text{R}_2\text{Sn}(\text{OOCR}')_2$ in a 1:1 mole ratio. The Mössbauer spectrum of a single compound should be relatively simple while the Mössbauer spectra of a mixed crystal would be expected to be a superposition of the two constituents. Mössbauer parameters for

$(\text{CH}_3)_2\text{SnCl}(\text{OOCR})$ are listed in Table XXV. Comparison with the Mössbauer parameters for the respective $(\text{CH}_3)_2\text{Sn}(\text{OOCR})_2$ shows only a small shift in quadrupole splitting and chemical shift. Inspection of the Mössbauer spectra of $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$, Appendix 11, shows only two symmetric peaks ($\Delta E = 3.81 \text{ mm/sec.}$; $\delta_0 = 1.39 \text{ mm/sec.}$) with no trace of $(\text{CH}_3)_2\text{SnCl}_2$ ($\Delta E = 3.41 \text{ mm/sec.}$; $\delta_0 = 1.53 \text{ mm/sec.}$).⁴⁶ These data support the assumption that a single compound is present.

Inspection of Table XXV shows that both ΔE and δ_0 increase in going from $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_3)$ to $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$. This trend is similar to that found for compounds of the type $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OOCCH}_n\text{Cl}_{3-n})_2$ listed in Table XXXV. Such a trend is understandable since electron withdrawing groups would remove electron density from Sn(IV) causing δ_0 to increase in the direction associated with Sn(II) compounds.^{148a}

4) Infrared Spectroscopy

General: The infrared spectra of $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$ and $(\text{C}_6\text{H}_5)_2\text{SnCl}(\text{OOC}_6\text{H}_5)$ are shown in Figures 41-44. The preparation of the latter compound has been reported previously.¹⁶⁰ Although the infrared spectra in the two cases are somewhat similar, the physical properties are quite

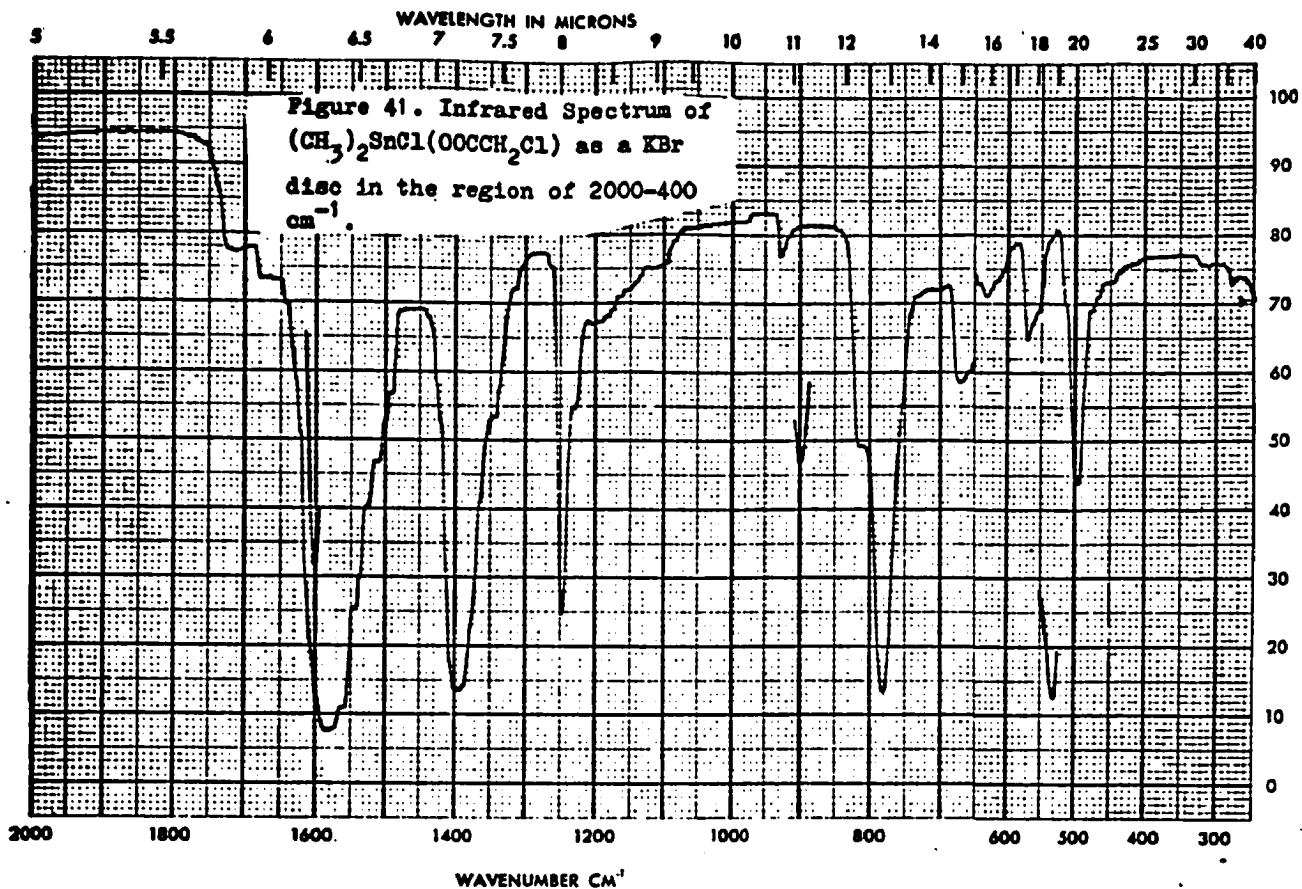
TABLE XXXV

Mössbauer Parameters for $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OOCCH}_n\text{Cl}_{3-n})_2$ ^a

R	ΔE	δ_o^b	References
3	3.50	1.34	158
2	3.56	1.46	159
1	3.73	1.54	159
0	4.00	1.60	159

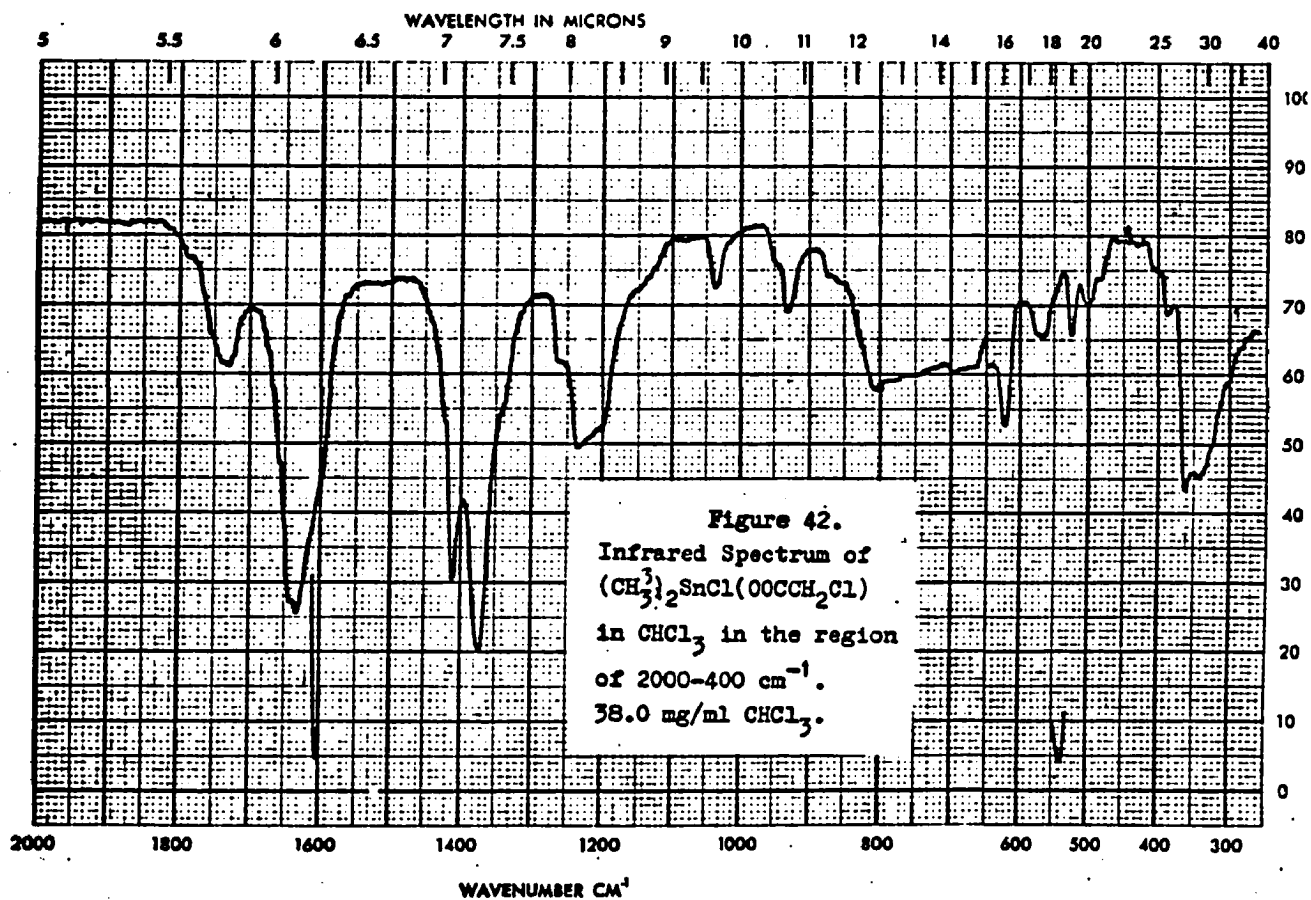
^a 78°K. ^b All data in mm/sec.; relative to BaSnO₃ ;

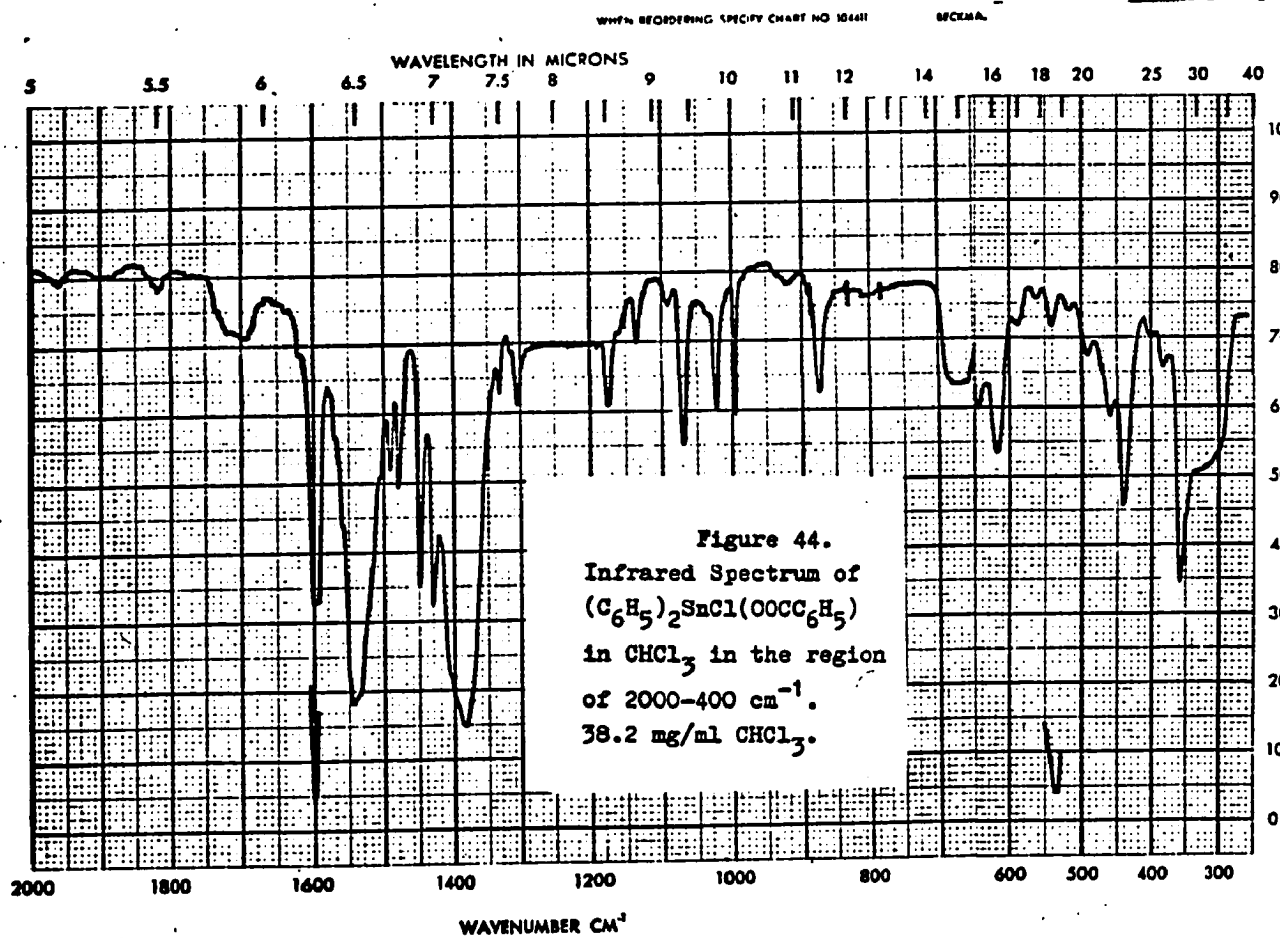
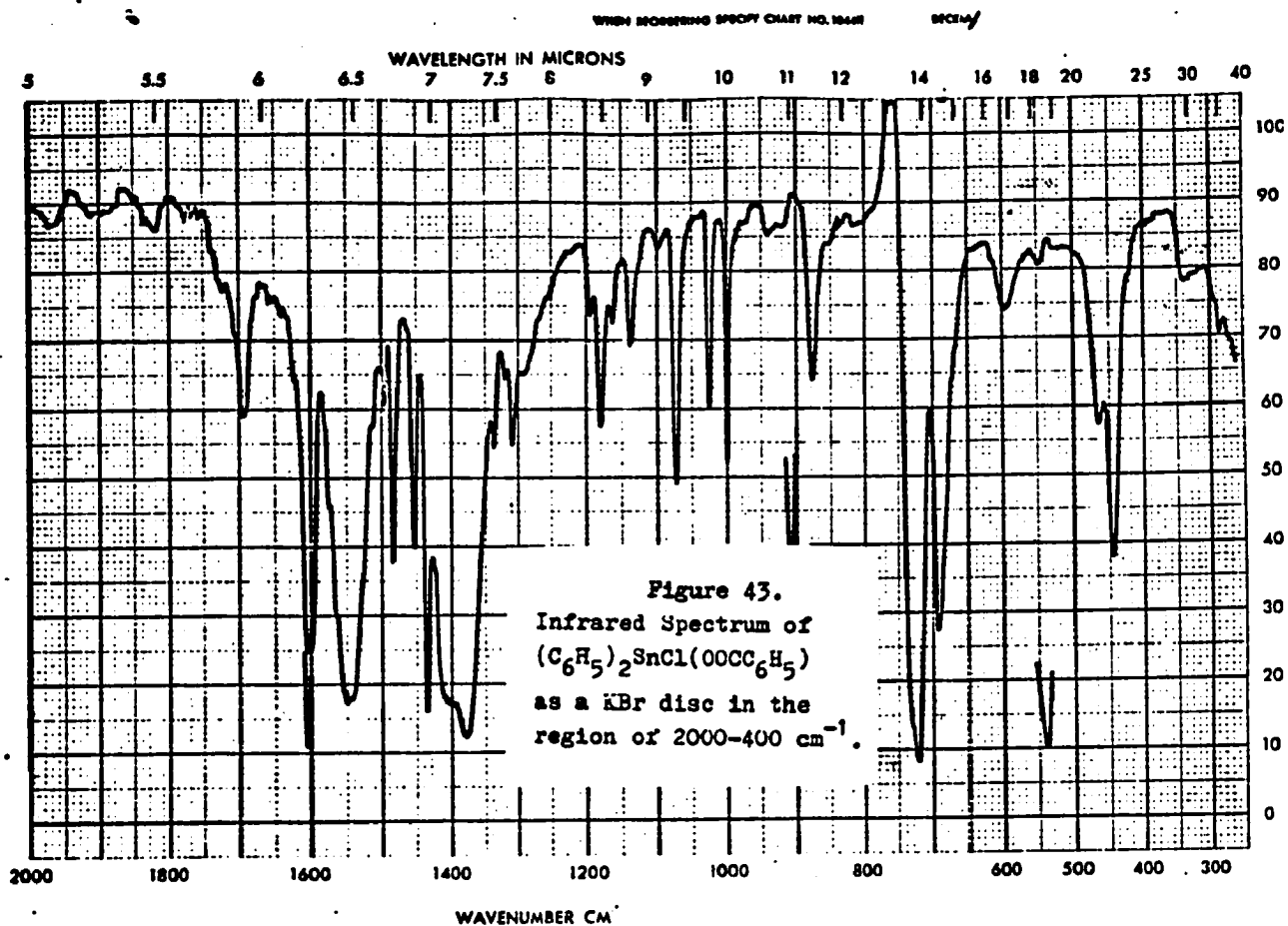
see reference 33, p. 338.



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different. For example, the compound was reported to decompose above 185° while the present study found a melting point of $72.5 - 73.5^{\circ}$ (Table XXII). In addition, the compound was reported to exist in two forms, a liquid and a solid form; while the present investigation only found evidence for a solid form. It is probable that the previous study of $(C_6H_5)_2SnCl(OOCC_6H_5)$ produced a polymeric form since the synthetic approach involved reflux at high temperatures for long periods, yielding a product with a high melting point and a high molecular weight (1382 vs. 429 for a monomer¹⁶⁰).

COO Region: The positions of the asymmetric and symmetric COO stretching vibrations of these and similar compounds are listed in Table XXVI. The separation, Δ , of these frequencies for the diorganotin halide carboxylates are tabulated in Table XXVII along with the "B" and "C" ratios (see above). Comparison with the values for the respective diorganotin bis(carboxylates) Table XXXI, shows a general drop in the "B" ratio and a general increase in the "C" ratio for $R_2SnCl(OOCR')$. However, except for two instances, the values are in the same ranges found for the "B" and "C" ratios for the other organotin carboxylates studied.

The very low "B" ratio (0.52) of $(\text{CH}_3)_2\text{SnCl}(\text{OOC}_2\text{H}_5)$ may be due to an inaccurate assignment of the symmetric COO stretching vibration, since the band is masked somewhat by a band due to the C_2H_5 group.⁸¹ The very low "C" ratio (0.89) of $(\text{C}_6\text{H}_5)_2\text{SnCl}(\text{OOC}_6\text{H}_5)$ may be caused by the decomposition of the compound in solution--consistent with the known instability of phenyltin carboxylates in solution.^{146,159} An alternate possibility is that this compound still contains a bridging carboxyl group since its low "C" ratio falls in the range corresponding to a bridging carboxyl group (see above). This latter possibility could be checked by molecular weight determination.

Sn-C and Sn-Cl Region: The methyltin chloride carboxylates studied have two absorptions assigned to the asymmetric and symmetric tin-carbon stretch (Table XXVIII). The tin-phenyl stretching vibrations were not detected since they usually occur in the range of $270\text{--}226\text{ cm}^{-1}$,¹⁶¹ below the range of the infrared spectrophotometers used in this work. Table XXVII also lists the Sn-Cl stretch which, for the limited number of compounds studied, falls within the range expected for the Sn-Cl stretch.^{162,163}

5) Conclusions

The present study indicates that, depending upon the nature of R in $R_2SnCl(OOCR')$, diorganotin halide carboxylates may be isolated in the solid. The structure of these compounds were found by NMR and infrared spectroscopy to be five-coordinate polymers in the solid state with bridging carboxyl groups. Internally chelating carboxyl groups were indicated in solution, corresponding to a monomeric structure. For the dimethyltin compounds the present investigation found two infrared-active Sn-C absorptions, indicating a non-linear C-Sn-C moiety. Because of the limited scope of the present study, however, we were not able to ascertain whether both methyl groups are in equatorial positions (Figure 3-c) as predicted by theory (see Chapter II).

CHAPTER VI

SUMMARY AND EXTENSIONS

A. Dimethyltin bis(carboxylates).

In the present investigation it was found that the dimethyltin bis(p-substituted benzoates) studied show a Mössbauer effect at room temperature. They have molecular weights which increase with increasing concentration. In addition, their infrared spectra show Δ -ratios in the solid which fall in the "B" range. Thus, these compounds are polymeric in the solid state (Figure 45) with bridging carboxyl groups.

On the other hand, studies of these compounds in solution found a constant chemical shift, τ (Sn-CH_3), and a very small range for the tin-methyl coupling constant, $J(^{119}\text{Sn-C-H})$. Molecular weight studies at infinite dilution corresponded to monomers. Their infrared spectra show Δ -ratios in solution which are in a higher range than the corresponding "B" range. There is good evidence that the polymeric structures of the dimethyltin bis(p-substituted benzoates) in the solid break down in solution forming monomers with internally chelating carboxyl groups (Figure 32).

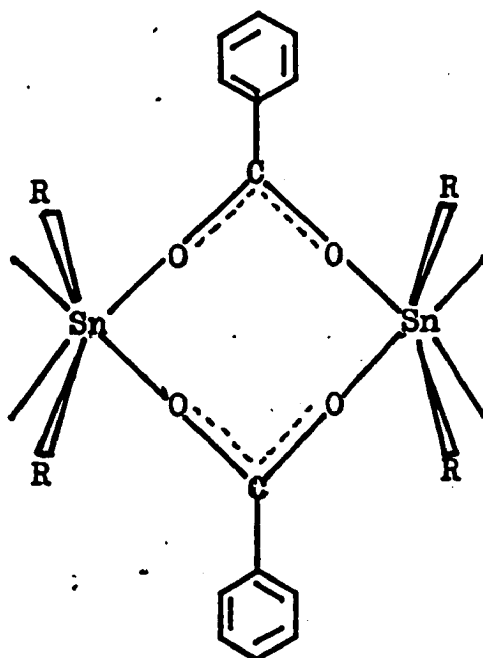


Figure 45. Proposed polymeric structure for dimethyltin bis(benzoates) in the solid.

The infrared spectra in the solid and solution also show evidence of two Sn-C bands, indicating a non-linear C-Sn-C moiety.

In comparing the Mössbauer data at 77°K with the donor properties of the carboxylate linear relationships were found between δ_o and σ_p (Figure 33) and between ΔE and σ_p (Figure 34). This indicated that the polarity of the tin-oxygen bonds varies with the donor strength of the carboxylate. In view of the non-linearity of the C-Sn-C moiety in these compounds, it would seem likely that the C-Sn-C angle should vary with the donor properties of the carboxylate. X-ray studies of these dimethyltin bis(benzoates) would be invaluable in ascertaining the validity of this proposal.

Contrary to the conclusion of many authors (see Chapter I⁶⁷⁻⁷²) the present study has found infrared spectroscopy useful in distinguishing between the different modes of bonding of a carboxyl group bonded to a non-transition metal. When the separation of $\nu_{\text{asym.}}$ and $\nu_{\text{sym.}}$ (COO) in the infrared spectra of organotin carboxylates were compared with the analogous separation of the corresponding sodium carboxylates, the value of the ratios were found to vary. Organotin carboxylates in the solid had a range of 0.94-1.33 ("B"ratio); while in solution they had a range of 1.38-1.61 ("C"ratio).

Independent evidence suggested that these compounds are polymeric in the solid and monomeric in solution. Therefore, the former range should correspond to a bridging carboxyl group while the latter range should correspond to an internally chelating carboxyl group. This empirical relationship should be checked by single crystal x-ray data of the dimethyltin bis(carboxylates) as well as by infrared studies of the COO stretching vibrations of carboxylate salts in solution.

To ascertain the scope of the empirical relationships found for bridging and internally chelating carboxyl groups, it is proposed to study the infrared spectra and structure of other non-transition metal carboxylates as well as para-substituted thio- and dithiocarboxylate derivatives of dimethyltin. The latter series would also show whether the para-substituent is able to transfer electron density to or from the Sn-CH_3 bonds via the tin-sulfur bonds.

The donor properties of the carboxylate appeared to influence the "C" ratio as shown by the linear relationship between the pK_a of the carboxylate and the values of the "C" ratio. In considering this relationship as well as those between δ_o , ΔE , and σ_p , it should prove interesting to compare the values of the "C" ratio with the Mössbauer parameters of frozen solutions.

According to some authors,^{17,76} the Sn-O bond strength should be effected by subtle differences in the donor properties of the carboxylate. However, assignment of the Sn-O bond in the present work was uncertain. Judging from previous work,¹⁶⁴ it would be profitable to synthesize and study the infrared spectrum of ¹⁸O-labeled $(\text{CH}_3)_2\text{Sn}(\text{OOC}^6\text{H}_5)_2$ or $(\text{CH}_3)_2\text{Sn}(\text{OOCCH}_3)_2$ and compare it with the analogous non-labeled compound to determine the exact position of the Sn-O stretching band. A shift of 1-2% is expected in this band while a shift of about 8 cm^{-1} is expected in the bending vibration of this bond.¹⁶⁵ Assuming that the positions of the tin-oxygen stretching vibrations are found to vary between compounds, comparisons could be made between the tin-oxygen bond strength and both the Mössbauer parameters of the dimethyltin bis(carboxylates) and the mode of coordination of the carboxyl group.

B. Exchange Reactions.

This study is the first report of an exchange between diorganotin dihalides and triorganotin carboxylates. The exchange reaction is important in understanding the chemistry of five-coordinate diorganotin halide carboxylates since $\text{R}_2\text{SnCl}(\text{OOCR}^{\prime\prime})$ may be synthesized without prior preparation of six-coordinate organotin compounds. In addition, the

reaction system affords the opportunity to study the mechanism of formation of five-coordinate diorganotin halide carboxylates and their disproportionation in solution into four- and six-coordinate organotin carboxylates.

The existence of a free carbonyl in solutions of triorganotin carboxylates^{7,126,127} suggests that reactions between R_2SnCl_2 and $R'_3Sn(OOCR'')$ are initiated by attack of the free carbonyl group on R_2SnCl_2 in a Lewis acid - Lewis base type of reaction. Both tin atoms in the proposed intermediate (Figure 40) expand their coordination numbers to five. This, in turn, breaks apart into the apparently more stable R'_3SnCl and $R_2SnCl(OOCR'')$.

This mechanism could be confirmed by kinetic studies. Since the present series of reactions proceed very rapidly at room temperature, low temperature studies might be feasible. An alternate mechanism involving the equilibrium of R_2SnCl_2 and $R_2Sn(OOCR'')_2$ was deemed unlikely since these reactions were not found to be reversible.

The scope of these reactions should be extended to other organotin halides such as CH_3SnCl_3 , as well as to other chelates, such as thio- and dithiocarboxylates, to test the relative stability of the reactants vs. products.

In addition, trimethyltin oxinate should be used. If it did not react with R_2SnCl_2 , this would be additional evidence for its proposed five-coordinate structure in solution¹⁹ as well as evidence for the reaction proceeding through initial attack of a free carbonyl group.

Besides synthesizing new organometallic compounds it is proposed to investigate systems such as R_2SnX_2 with $R_3M(\text{chelate})$ (where $M = \text{Si, Ge, or Pb}$) with the intention of studying the relative stability of organo-Group IV-metal chelates by their tendency to react with R_2SnX_2 and $R_2SnX(\text{chelate})$.

C. Diorganotin halide carboxylates.

One of the initial objectives of the present study was to investigate the structure and properties of compounds of the type $(\underline{p}\text{-XC}_6\text{H}_4\text{COO})SnY(\text{CH}_3)_2$ (where $X = \text{halide, CH}_3, \text{CH}_3\text{O, NO}_2, \text{etc.}; Y = \text{halide}$). However, attempts to isolate these compounds were unsuccessful. The best results were obtained with $(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{COO})SnCl(\text{CH}_3)_2$ where a small amount of a sharp melting white powder was formed with a slightly low tin analysis. (Table XXIII) In view of the exchange reactions involving R_2SnX_2 and $R'_3Sn(\text{OOCR:})$, it is proposed to make $(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{COO})SnCl(\text{CH}_3)_2$ by reaction of $(\text{CH}_3)_2SnCl_2$ with $(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{COO})Sn(\text{CH}_3)_3$.

In studying the causes of the instability of diorganotin halide carboxylates similar compounds, such as dimethyltin chloride monochloroacetate and diphenyltin chloride benzoate, were isolated. Thus, only five coordinate methyltin benzoates appear to be unstable.

CHAPTER VII

EXPERIMENTAL

Materials: All solvents used in this investigation were reagent grade, spectrophotometric grade, or were purified according to standard methods.¹⁶⁶ Dimethyltin oxide, dimethyltin dichloride, diphenyltin dichloride, trimethyltin chloride, triphenyltin chloride, and triphenyltin acetate were obtained from M & T Chemicals, Inc., Rahway, N. J. These compounds were purified as mentioned below. Dimethyltin dichloride, benzene, m.p. 106.5° , lit.¹⁶⁷ $107.5-108^{\circ}$; diphenyltin dichloride, ligroin, m.p. $40-41^{\circ}$, lit.¹⁶⁷ $42-44^{\circ}$; trimethyltin chloride, petroleum ether, m.p. 40° , lit.¹⁶⁸ 37° ; triphenyltin acetate, absolute ethanol, m.p. $123-124^{\circ}$, lit.¹⁶⁹ $120-122^{\circ}$. Triphenyltin chloride had m.p. 106° , lit.¹⁶⁹ $105.5-107^{\circ}$. Dimethyltin dibromide was obtained from Alpha Inorganics, Inc., Cambridge, Mass., m.p. $78-81^{\circ}$ lit.¹⁷⁰ $74-76^{\circ}$. Dimethyltin diiodide was obtained from Orgmet, Inc., Hampstead, N. H., m.p. $35-37^{\circ}$, lit.¹⁷⁰ 43° . The last three compounds were used without further purification.

The substituted benzoic acids were obtained from commercial sources and were used without further purification except as mentioned below. Sources and properties were as follows: p-aminobenzoic acid, Brooklyn College Stockroom, water/ethanol (1:1, v/v), m.p. 185-186[°], lit.¹⁷¹ 186-187[°]; o-toluic acid, Cowles Chemical Co., m.p. 106-107[°], lit.¹⁷² 104-105[°]; p-cyanobenzoic acid, Pfaltz and Bauer Chemical Co.; the p-Cl, p-CH₃, p-CH₃O, and p-NO₂ benzoic acids were Eastman White Label. Monochloroacetic acid, Fisher Certified Reagent; dichloroacetic acid, M. C. & B. practical; benzoic acid and trichloroacetic acid, Baker Analyzed. Sodium benzoate was U.S.P. Grade.

Melting Points: Melting points were determined by use of sealed capillaries in an oil bath up to about 210[°] and in a Mel-Temp hot stage for higher temperatures. Use was also made of a Nalge Company hot stage at both temperature ranges, placing the compounds between glass plates. All melting points are uncorrected. The hot stages generally gave values of about 2 degrees above the values obtained using the oil bath.

Analysis: All C, H, N, and Cl analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Tin was determined gravimetrically in this laboratory

as SnO_2 by degrading the compounds in H_2SO_4 according to the method of Okawara, Webster, and Rochow⁵⁹ as modified by Okawara and Wada.¹⁷³

Molecular Weights: Molecular weights were determined by means of a Mechrolab Vapor Pressure Osmometer. The Osmometer was first calibrated against a "known" molecular weight ($(\text{C}_6\text{H}_{11})_3\text{SnCl}$ in benzene and $(\text{C}_6\text{H}_{11})_4\text{Sn}$ in chloroform) by running at four concentrations and obtaining an average ΔR for each concentration. A plot of $\Delta R/C$ against C was made, and extrapolation to "zero" concentration gave a $(\Delta R/C)C \rightarrow 0$, which when multiplied by the molecular weight of the standard gave a "K" factor. The compounds were then run at similar concentrations and plotted to give $(\Delta R/C)C \rightarrow 0$, which when divided into K gave the molecular weight. Since the plot was not exactly parallel to the concentration axis, the molecular weights appeared to vary with concentration, since a different K was obtained at each concentration. However, it should be noted that the standards also are not parallel to the concentration axis.

NMR Spectra: Nuclear magnetic resonance spectra were determined with a Varian Associates A60A spectrometer at various temperatures (-55° to 40°C). TMS ($\tau = 10$ ppm) was used as an internal standard. Calibration was effected by

the CHCl_3 peak in CDCl_3 . Except where noted, all spectra were run at a sweep width of 500 Hz.

Mössbauer Spectra: Mössbauer spectra were obtained in the Department of Chemistry, The Catholic University of America, Washington, D. C., and in the National Bureau of Standards, Washington, D. C., at room temperature using both Pd_3Sn and BaSnO_3 as the source and at liquid nitrogen temperature using only BaSnO_3 as the source. The Mössbauer spectra at 77°K are shown in Appendixes 1-11. The solid line represents the Lorentzian curve. The circles represent the counts. In plotting the data, the following information was used:

Calibration: -0.0711 mm/sec/channel
Positive velocity: 0--96.02 channels
Negative velocity: 96.02--200 channels

Infrared Spectra: The infrared spectra were measured with a Beckman IR-10 double beam spectrophotometer or with a Perkin Elmer - 21 double beam spectrophotometer between potassium bromide or cesium bromide plates. Spectra were run as nujol mulls, KBr discs, or as solutions in chloroform or benzene. Spectra of compounds in solution were run against pure solvent using matched potassium bromide cells having a 0.2 mm path length. Calibration was effected with

polystyrene. The nomenclature of the assignments in Appendixes 12-22 is from Whiffen,¹⁷⁶ while the actual assignments were based upon comparison with the respective sodium salts as well as upon comparison with the works of Katritzky,¹⁷⁷⁻¹⁷⁹ Dillard,⁶⁰ Lohmann,⁸¹ Kawasaki,⁷⁶ Lindsey,¹⁵³ and Okawara.¹⁸⁰

Syntheses

Dimethyltin bis(benzoate) : $(C_6H_5COO)_2Sn(CH_3)_2$

Procedure A: The procedure of Okawara¹³⁸ was used with certain modifications, as follows: Concentrated ammonia was added dropwise to a solution of 12 g (0.055 mole) dimethyltin dichloride and 18 g (0.146 mole) benzoic acid in about 1,500 ml water with stirring until the addition of one drop of ammonia formed no additional precipitate. The white precipitate was filtered, washed twice with hot water, once with a small amount of chilled methanol, and dried overnight in a vacuum desiccator. The dried product was treated at room temperature with about 70 ml methanol containing a small amount of benzoic acid. The slurry was filtered and the filtrate was condensed to one third its original volume and cooled. This procedure yielded 7.85 g (37%) of large, clear, colorless, rectangular crystals, m.p. 161.5-163°; lit.¹³⁹ 160-162°, 162-164°, ¹³⁸ (Found; Sn, 29.73. Calcd. for $C_{16}H_{16}O_4Sn$: Sn, 30.35%).

Procedure B: The procedure of Razuvaev¹³⁹ was used.

A solution of 1.0 g (0.0018 mole) tetramethyl 1,3-dibenzoate distannoxane, $[(CH_3)_2Sn(OOCC_6H_5)]_2O$, and 0.50 g (0.0041 mole) benzoic acid in 15 ml benzene was refluxed for one hour in the presence of 1.0 g of anhydron (anhydrous magnesium perchlorate). The reaction mixture was then allowed to stand at room temperature overnight. The solution was again heated, filtered, and hot heptane added until the solution turned turbid. When the mixture was cooled an intractable oil was obtained. Several additional attempts were made using this procedure--always with the same results.

Procedure C: A solution of 8.4 g (0.051 mole) dimethyltin oxide and 12.5 g (0.102 mole) benzoic acid in 250 ml benzene was refluxed for three hours. After distilling off most of the solvent the solution was filtered hot, condensed to about 50 ml, and allowed to cool overnight at room temperature. This procedure yielded 13.9 g (70%) of crude product in two crops. Recrystallization of the crude product from benzene afforded 10.1 g of pure $(C_6H_5COO)_2Sn(CH_3)_2$, m.p. 161-163°. Further condensation of the filtrate yielded an additional 2.1 g with the same m.p. (Found: Sn, 30.48. Calcd. for $C_{16}H_{16}O_4Sn$: Sn, 30.35%).

Dimethyltin bis(p-chlorobenzoate) : $(\text{p-ClC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$

Procedure A: Concentrated ammonia was added dropwise to a solution of 4 g (0.018 mole) dimethyltin dichloride and 6.43 g (0.041 mole) p-chlorobenzoic acid in 200 ml methanol until precipitation was complete. The white precipitate formed was filtered and dried overnight in a vacuum desiccator. Treatment with hot methanol containing a small amount of the acid yielded only the distannoxane, $[(\text{p-ClC}_6\text{H}_4\text{COO})\text{Sn}(\text{CH}_3)_2]_2\text{O}$ (Found: Sn, 36.17. Calcd. for $\text{C}_{18}\text{H}_{20}\text{Cl}_2\text{O}_4\text{Sn}_2$: Sn, 37.8%).

Procedure B: A solution of 11.0 g (0.176 mole) tetramethyl 1,3-bis(p-chlorobenzoate) distannoxane, $[(\text{p-ClC}_6\text{H}_4\text{COO})\text{Sn}(\text{CH}_3)_2]_2\text{O}$, and 5.5 g (0.0351 mole) p-chlorobenzoic acid in 33 ml p-dioxane and 187 ml benzene was refluxed for two hours under nitrogen in the presence of 13.8 g of anhydrous. The reaction was let stand at room temperature overnight. The solution was then heated, filtered hot, condensed, and hot heptane added dropwise until a slight turbidity persisted. Cooling yielded 7.0 g (43%) of clear, shiny plates. Two recrystallizations from heptane/benzene yielded 1.7 g of dimethyltin bis (p-chlorobenzoate), m.p. 201.5-203° (Found: Sn, 25.70. Calcd. for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_4\text{Sn}$: Sn, 25.81%).

Procedure C: A solution of 8.4 g (0.051 mole) dimethyltin oxide and 16 g (0.102 mole) p-chlorobenzoic acid in 250 ml benzene was refluxed for two hours. The solution was condensed filtered hot, and cooled to yield 21.7 g (93%) of product in two crops. Recrystallization from benzene gave 19.7 g of dimethyltin bis(p-chlorobenzoate), m.p. 201-203.5° (Found: Sn, 25.68. Calcd. for $C_{16}H_{14}Cl_2O_4Sn$: Sn, 25.81%). The major advantage of this method appears to be the greater yield compared with the results from Procedure B.

Procedure D: A slurry of 1.6 g (0.010 mole) p-chlorobenzoic acid in 30 ml water was neutralized to a phenolphthalein end point with 6 N sodium hydroxide. Addition of this solution to 2.2 g (0.010 mole) dimethyltin dichloride in 50 ml benzene resulted in the immediate formation of a white precipitate. The slurry was stirred vigorously for thirty minutes at room temperature. An infrared spectrum of the dried white product was superimposable on the infrared spectrum of the original p-chlorobenzoic acid. The organic layer was filtered, condensed, hot heptane added, and cooled. This procedure yielded two crops of crystals. The infrared spectrum of the first crop indicated the presence of both the acid and the desired product. The infrared spectrum of the second crop indicated that it was mainly tetramethyl 1,3-bis(p-chlorobenzoate) distannoxane.

Dimethyltin bis(p-aminobenzoate) : $(\text{p-NH}_2\text{C}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$

Procedure A: Concentrated ammonia was added dropwise to a solution of 4 g (0.018 mole) dimethyltin dichloride and 6.7 g (0.049 mole) p-aminobenzoic acid in 550 ml hot water until precipitation was complete. The light tan precipitate was filtered, washed with a small amount of methanol, and dried overnight in a vacuum dessicator. Trituration of this with about 35 ml methanol containing a small amount of the acid at room temperature yielded 0.13 g of small tan crystals, m.p. 247-249°. Analysis showed this to be tetramethyl 1,3-bis (p-aminobenzoate) distannoxane, $[(\text{p-NH}_2\text{C}_6\text{H}_4\text{COO})\text{Sn}(\text{CH}_3)_2]_2\text{O}$ (Found: Sn, 37.55. Calcd. for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_4\text{Sn}_2$: Sn, 40.52%).

Procedure B: A solution of 1.16 g (0.0020 mole) tetramethyl 1,3-bis(p-aminobenzoate) distannoxane and 0.51 g (0.0037 mole) p-aminobenzoic acid in 30 ml chlorobenzene was refluxed for two hours under nitrogen in the presence of 1.25 g anhydron. This was allowed to stand at room temperature overnight. The hot solution was then filtered, condensed to about one half the original volume, and cooled. This yielded 1.02 g (61%) light yellow plates, of dimethyltin bis(p-aminobenzoate). Recrystallization from chlorobenzene

and washing with heptane afforded a product with m.p., 226-227° (Found: Sn, 28.11. Calcd. for $C_{16}H_{18}N_2O_4Sn$: Sn, 28.19%).

Procedure C: A solution of 8.4 g (0.051 mole) dimethyltin oxide and 14.0 g (0.102 mole) p-aminobenzoic acid was refluxed for two hours in 250 ml chlorobenzene. The solution was filtered hot, condensed to half the original volume, and cooled. Filtering the yellow-brown plates, washing with several small portions of heptane, and drying in a vacuum desiccator yielded 16.2 g (75%) of product. Recrystallization from chlorobenzene gave 15.6 g of dimethyltin bis(p-aminobenzoate), m.p. 226-228° (Found: Sn, 27.99. Calcd. for $C_{16}H_{18}N_2O_4Sn$: Sn, 28.19%).

Dimethyltin bis(p-nitrobenzoate) : (p-NO₂C₆H₄COO)₂Sn(CH₃)₂

Procedure C: A solution of 0.84 g (0.00051 mole) dimethyltin oxide and 1.71 g (0.0102 mole) p-nitrobenzoic acid was refluxed in 50 ml chlorobenzene for 2.5 hours. The solution was filtered hot, condensed to about half the original volume, and cooled. This yielded 2.15 g (88%) of a pale yellow-green powder which was washed with heptane and air-dried. Recrystallization from chlorobenzene yielded 1.86 g of dimethyltin bis(p-nitrobenzoate), m.p. 281-282° (Found: Sn, 24.62. Calcd. for $C_{16}H_{14}N_2O_8Sn$: Sn, 24.68%).

Dimethyltin bis (p-methoxybenzoate) : $(\text{p-CH}_3\text{OC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$

Procedure C: A solution of 0.84 g (0.0051 mole) dimethyltin oxide and 1.55 g (0.0102 mole) p-anisic acid was refluxed for two hours in 25 ml chlorobenzene. The solution was filtered hot, condensed to about half the original volume, and hot heptane added dropwise until the volume was approximately doubled. After standing at room temperature overnight the mixture was filtered and the precipitate was washed with heptane to yield 1.87 g (81%) of small, shiny cream colored plates. Recrystallization from chlorobenzene/heptane (1:1, v/v) gave 1.47 g of pure dimethyltin bis (p-methoxybenzoate), m.p. 171-173° (Found: Sn, 26.26. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_6\text{Sn}$: Sn, 26.31%).

Dimethyltin bis(p-toluate) : $(\text{p-CH}_3\text{C}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$

Procedure C: A solution of 0.84 g (0.0051 mole) dimethyltin oxide and 1.39 g (0.0102 mole) p-toluic acid was refluxed for two hours in 25 ml benzene. The solution was filtered hot, condensed to about half the original volume, and the volume of this solution was doubled by the addition of hot heptane. Cooling in the refrigerator overnight yielded 1.85 g (87%) of small colorless crystals. Drying in a drying pistol yielded a product with m.p. 126-128°. Recrystallization from benzene/heptane (1:2) yielded 1.02 g

large, clear, colorless, diamond-shaped crystals of dimethyltin bis (p-toluate) which formed at room temperature. After drying in a drying pistol the product had a m.p. of 126-129° (Found: Sn, 28.73. Calcd. for $C_{18}H_{20}O_4Sn$: Sn, 28.32%).

Dimethyltin bis (p-cyanobenzoate) : $(p-CNC_6H_4COO)_2Sn(CH_3)_2$

Procedure C: A solution of 0.84 g (0.0051 mole) dimethyltin oxide and 1.50 g (0.0102 mole) p-cyanobenzoic acid was refluxed in 50 ml chlorobenzene for two hours. The solution was then condensed, filtered, and further condensed to about one third its original volume. Cooling caused the immediate formation of a mass of crystals. This slurry was diluted to a volume of 35 ml, heated to boiling, and cooled in the refrigerator overnight. Pale-orange crystals were obtained. These were washed with heptane and dried in a drying pistol to yield 2.13 g (96%), m.p. 238-242° (Found: Sn, 26.87. Calcd. for $C_{18}H_{14}N_2O_4Sn$: Sn, 28.46%).

Dimethyltin bis (o-toluate) : $(o-CH_3C_6H_4COO)_2Sn(CH_3)_2$

Procedure C: A solution of 0.84 g (0.0051 mole) dimethyltin oxide and 1.40 g (0.0102 mole) o-toluic acid in 20 ml benzene was refluxed for two hours. The hot solution was filtered, half the solvent distilled off, and

replaced with hot heptane. Cooling to room temperature yielded 1.70 g (80%) of small cream-colored crystals of dimethyltin bis (o-toluate), m.p. 142-144° (Found: Sn, 28.31. Calcd. for $C_{18}H_{20}O_4Sn$: Sn, 28.32%).

Dimethyltin bis (monochloroacetate) : $CH_3)_2Sn(OOCCH_2Cl)_2$

Procedure C: A solution of 0.84 g (0.0051 mole) dimethyltin oxide and 0.97 g (0.0102 mole) monochloroacetic acid in 25 ml benzene was refluxed for about 2.5 hours. The hot solution was filtered, condensed, and cooled to room temperature. Almost immediately long, thin, needle-like crystals began to form. The crystals were filtered under a stream of nitrogen to yield 1.31 g (77%) of thin white needles of dimethyltin bis (monochloroacetate), m.p. 165-167°; lit.¹⁴³ 162-165° (Found: Sn, 35.52. Calcd. for $C_6H_{10}Cl_2O_4Sn$: Sn, 35.35%). Upon prolonged standing in air the shape of these crystals changed into small squares having a m.p. of 250° (probably the tetramethyl 1, 3-distannoxane). A similar decomposition was noted when a benzene solution of the compound was left standing for several days.

Attempts to synthesize dimethyltin bis (dichloroacetate) and dimethyltin bis (trichloroacetate) by this method only yielded the respective tetramethyl 1,3-distannoxane.

Syntheses of sodium salts of parasubstituted acids

Sodium salts of the various benzoic acids were prepared by reacting the respective acids with sodium hydroxide solution. A typical example follows: A slurry of 0.5137 g p-nitrobenzoic acid and 22.10 ml (0.50 ml excess) of 0.1409 N aqueous sodium hydroxide solution was stirred at room temperature until the solid acid dissolved. This solution was then evaporated to a very small volume. On standing clear yellow plates formed. These were dried first in air and then in a drying pistol. An infrared spectrum of each salt did not exhibit any of the bands in region of $3600-2400\text{ cm}^{-1}$ characteristic of the free carboxylic acid.¹⁷⁴ Other salts prepared by this procedure were p-ClC₆H₄COONa, p-CH₃OC₆H₄COONa, p-NH₂C₆H₄COONa, p-CH₃C₆H₄COONa, and p-CNC₆H₄COONa.

Dimethyltin chloride monochloroacetate : (CH₃)₂SnCl(OOCCH₂Cl)

A solution of 0.55 g (0.0025 mole) dimethyltin dichloride in 7 ml benzene was added, dropwise, to a solution of 0.84 g (0.025 mole) dimethyltin bis (monochloroacetate) in 11 ml benzene while stirring. After standing at room temperature for about an hour, small, rod-like, colorless crystals formed. This yielded a first crop, 0.82 g, m.p. 126.5-128° and a second crop, 0.43 g, m.p. 119-121° (90%). Analysis of the

first crop was as follows: (Found: Sn, 42.86. Calcd. for $C_{48}H_{82}Cl_2O_2Sn$: Sn, 42.74%).

Trimethyltin benzoate : $(CH_3)_3Sn(OOCC_6H_5)$

This was made according to the interfacial polymerization technique.¹⁴⁰ A solution of 9.95 g (0.050 mole) trimethyltin chloride in 250 ml dichloromethane was added dropwise over 2.5 hours with vigorous stirring to a solution of 7.20 g (0.050 mole) sodium benzoate in 150 ml distilled water cooled to 0°. After stirring for an additional ten minutes the organic layer was separated and dried with anhydrous magnesium sulfate. Evaporation to a volume of 30 ml and cooling yielded 11.90 g (84%) of long, white crystals in two crops, m.p. 129.5-130°.

Trimethyltin monochloroacetate: $(CH_3)_3Sn(OOCCH_2Cl)$

A solution of 19.90 g (0.10 mole) trimethyltin chloride in 280 ml dichloromethane was added dropwise with strong stirring over three hours to a solution of 9.50 g (0.10 mole) monochloroacetic acid in 150 ml distilled water previously neutralized to phenolphthalein with sodium hydroxide (10N) and kept at 0°. The organic layer was separated and dried with anhydrous magnesium sulfate. Evaporation to a volume of about 50 ml and cooling yielded 4.68 g of small white

needles, m.p. 142.5-143.5°; lit.¹⁵⁰ 143-145. Further condensation afforded two more crops totaling 2.60 g, m.p. 142-143° (28% yield overall). The properties of this compound were in agreement with the soluble form reported by Simons and Graham.¹⁵⁰

Triphenyltin benzoate : $(C_6H_5)_3Sn(OOCC_6H_5)$

A solution of 19.3 g (0.05 mole) triphenyltin chloride in 150 ml dichloromethane was added dropwise over one hour to a solution of 7.20 g (0.05 mole) sodium benzoate in 150 ml distilled water kept at 0°. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated to a viscous gel. Upon standing overnight this gel formed a solid mass of white crystals, 20.34 g (97%), m.p. 82.5-83.5°; lit.¹⁴⁰ 82-84°.

Reactions of R_2SnCl_2 with $R'_3Sn(OOCR'')$

These reactions were, in most instances, run under two different conditions of mole ratios of reactants; a 1:1 mole ratio and a 1:2 mole ratio.

Dimethyltin dichloride with trimethyltin benzoate

A solution of 1.0 g (0.0045 mole) dimethyltin dichloride and 1.30 g (0.0045 mole) trimethyltin benzoate in 3 ml

chloroform was condensed and the volume doubled by addition of heptane. Cooling in the freezer yielded 0.85 g white crystals, m.p. 63-115°. The NMR spectrum of this product showed a J value of 77.8 Hz, indicating the presence of a five-coordinate tin species (see Table XXIV). Attempts at recrystallization resulted in the precipitation of colorless crystals with a m.p., 159-162°, and NMR spectrum ($J = 83.5$; $\tau(\text{Sn-CH}_3) = 8.86$) corresponding to dimethyltin bis(benzoate), m.p., lit.¹³⁹ 160-162°.

A solution of 1.0 g (0.00456 mole) dimethyltin dichloride and 2.60 g (0.00912 mole) trimethyltin benzoate in a 6 ml heptane-chloroform (1:1, v/v) was condensed until crystallization began, to yield 0.81 g of dimethyltin bis(benzoate). Further condensation of the filtrate afforded two more crops for an overall yield of 1.39 g (78%), m.p. 161-163°; lit.¹³⁹ 160-162°. Sublimation of the residue yielded 0.1 g trimethyltin chloride m.p. 36-37°; lit.¹⁶⁸ 40°.

Dimethyltin dichloride with trimethyltin monochloroacetate

A solution of 0.85 g (0.0039 mole) dimethyltin dichloride in 5 ml benzene was added to a hot solution of 1.00 g (0.0039 mole) trimethyltin monochloroacetate in 10 ml benzene. Evaporation of a portion of solvent and cooling yielded 0.77 g (72%) of small, colorless squares of dimethyltin chloride

monochloroacetate, m.p. 122-125°. Its NMR spectrum and m.p. were nearly identical with the product obtained from the reaction of dimethyltin dichloride and dimethyltin bis (monochloroacetate) (see above).

A solution of 0.42 g (0.00195 mole) dimethyltin dichloride and 1.00 g (0.0039 mole) trimethyltin monochloroacetate in 11 ml benzene was condensed. Cooling to room temperature yielded 0.49 g (76%) of dimethyltin bis (monochloroacetate), m.p. 166-168°; lit.¹⁴³ 162-165°. The NMR spectrum of this product was very nearly the same as that obtained for pure dimethyltin bis (monochloroacetate) synthesized from dimethyltin oxide and monochloroacetic acid.

Dimethyltin chloride monochloroacetate with trimethyltin monochloroacetate

A solution of 0.54 g (0.00195 mole) dimethyltin chloride monochloroacetate and 0.50 g (0.00195 mole) trimethyltin monochloroacetate in 11 ml benzene was condensed and cooled to room temperature to yield 0.51 g (78%) colorless needles of dimethyltin bis (monochloroacetate), m.p. 166-168°; lit.¹⁴³ 162-165°.

Attempted reversal reaction

A solution of 0.50 g (0.00149 mole) dimethyltin bis (monochloroacetate) and 0.89 g (0.00447 mole) trimethyltin

chloride in 5 ml benzene was condensed and cooled to yield 0.35 g colorless needles of crude dimethyltin bis (mono-chloroacetate), m.p. 155-160°; lit.¹⁴³ 162-165°. The NMR spectrum of this product showed the presence of a small amount of trimethyltin chloride (τ = 9.37 ppm).

Dimethyltin dichloride with tributyltin benzoate

To a solution of 1.00 g (0.00455 mole) dimethyltin dichloride in 5 ml chloroform was added, dropwise, 1.88 g (0.00455 mole) tri-n-butyltin benzoate. Some of the solvent was evaporated and the solution cooled to room temperature. Filtering and washing the resultant small, white needles with chilled heptane and chloroform yielded 0.27 g crude dimethyltin bis(benzoate); m.p. 149-152°, lit.¹³⁹ 160-162°. The NMR spectrum of the crude product showed a J value of 82.5 Hz, compared with a J value of 84.0 Hz for pure dimethyltin bis(benzoate).

Dimethyltin dichloride with triphenyltin acetate

A solution of 1.07 g (0.0049 mole) dimethyltin dichloride and 2.00 g (0.0049 mole) triphenyltin acetate in 21 ml chloroform was concentrated and cooled to room temperature. This yielded 0.91 g (77%) of dimethyltin chloride acetate, m.p. 182-184°, lit.¹⁸ 185-186°. The infrared spectrum of this product was superimposable with the infrared

spectrum of authentic dimethyltin chloride acetate.¹⁸

The NMR spectrum of a freshly prepared solution of 0.53 g (0.00245 mole) dimethyltin dichloride and 2.00 g (0.0049 mole) triphenyltin acetate in 15 ml chloroform showed a J value of 81.2 Hz, indicating the presence of dimethyltin bis(acetate) in solution. However, after evaporation of some solvent and cooling in the freezer, 0.12 g of crude dimethyltin chloride acetate was obtained, m.p. 178-179°, lit.¹⁸ 185-186°. Distillation of the residue afforded a mixture of dimethyltin bis(acetate) and some trimethyltin species as evidenced by the appearance of peaks at $\tau = 9.01$ and 9.20 ppm in the NMR spectra run in CDCl_3 .

Dimethyltin chloride acetate with triphenyltin acetate

A solution of 0.25 g (0.00205 mole) dimethyltin chloride acetate and 0.42 g (0.00205 mole) triphenyltin acetate in 6.5 ml chloroform was heated until all solids dissolved. A NMR spectrum showed the presence of dimethyltin bis(acetate) (J = 82.3 Hz). Evaporation of some solvent and cooling yielded 0.05 g of dimethyltin chloride acetate, m.p. 182-184°, lit.¹⁸ 185-186°. Further attempts to isolate dimethyltin bis(acetate) were not made.

Dimethyltin dichloride with triphenyltin benzoate

To a solution of 0.46 g (0.0021 mole) dimethyltin dichloride in 10 ml chloroform-hexane (1:3, v/v) was added 2.00 g (0.00425 mole) triphenyltin benzoate. The solvent of the clear solution was pumped off under vacuum until crystallization began. This yielded 0.99 g white crystals, m.p. 88-115°. Recrystallization of this and the filtrate (which solidified during filtration) from chloroform-hexane (1:1, v/v) yielded crystals with m.p., 88-130°. This was shown by NMR spectroscopy to be a mixture of dimethyltin bis (benzoate) and triphenyltin chloride. An attempted separation of the two products by vacuum sublimation was not successful.

Diphenyltin dichloride with trimethyltin benzoate

A solution of 1.21 g (0.0035 mole) diphenyltin dichloride in 10 ml ligroin was added to a solution of 1.00 g (0.0035 mole) trimethyltin benzoate in 15 ml ligroin. Removal of about 18 ml of solvent under vacuum and cooling in the freezer overnight yielded 1.33 g (88%) of a white powder of diphenyltin chloride benzoate, m.p. 71.5-73°. Recrystallization from ligroin with only a minimum of heating raised the m.p. to 72.5-73.5° (Found: Sn, 27.53. Calcd. for $C_{19}H_{15}ClO_2Sn$: Sn, 27.64%).

A solution of 1.21 g (0.0035 mole) diphenyltin dichloride in 10 ml ligroin was added to a solution of 2.00 g (0.0070 mole) trimethyltin benzoate in 30 ml ligroin. Evaporation of the solvent under vacuum until crystallization began and cooling resulted in 1.32 g (73%) of diphenyltin bis (benzoate), m.p. 115-119°. Two recrystallizations from ligroin with a minimum of heating afforded small white crystals, m.p. 116-118.5°; lit.¹⁴⁶ 116-117° (Found: Sn, 23.10. Calcd. for $C_{26}H_{20}O_4Sn$: Sn, 23.04%).

Attempts to synthesize dimethyltin chloride
(p-substituted benzoates)

The different types of reactions used in this investigation are listed in Table XXIII.

Dimethyltin chloride benzoate : $(C_6H_5COO)SnCl(CH_3)_2$

Reaction 1: A solution of 0.22 g (0.001 mole) dimethyltin dichloride and 0.39 g (0.001 mole) dimethyltin bis (benzoate) in 5 ml benzene was gently refluxed for 3 hours. A five-coordinate species in solution was indicated by a J value of 74.8 Hz. The volume was doubled by dropwise addition of heptane and cooled in the freezer to yield two types of crystals: amorphous lumps; 0.07 g, m.p. 225.5-228°

(Found: Sn, 47.77. Calcd. for $(C_6H_5COO)SnCl(CH_3)_2$:
Sn, 37.16%; Calcd. for $[(C_6H_5COO)ClSn(CH_3)_2]_2O$: Sn, 42.71%)
and colorless rods; 0.07 g, m.p. 168-171°. This is close to
that for dimethyltin bis(benzoate), m.p. 162-164°. ¹³⁸

Two other similar attempts yielded either an intractable mixture or dimethyltin bis(benzoate). A related approach involved evaporating off the entire solvent and taking up the residue in a solvent such as carbon tetrachloride. This product had a melting point, mixed melting point, and infrared spectrum which showed it to be dimethyltin bis(benzoate). Further condensation of the filtrate yielded the tetramethyl 1,3-distannoxane, $[(C_6H_5COO)Sn(CH_3)_2]_2O$, as shown by infrared spectroscopy. Dimethyltin bis(benzoate) and the tetramethyl 1,3-distannoxane were obtained even when dimethyltin dibromide was used with this reaction.

Reaction 2: A solution of 1.61 g (0.0132 mole) benzoic acid in 5 ml ethanol was added to a solution of 2.90 g (0.0132 mole) dimethyltin dichloride in 5 ml ethanol. About half of the solvent was removed under vacuum and the solution cooled. This yielded 0.55 g of colorless needles with a complex m.p. An infrared spectrum showed that this product contained free acid.

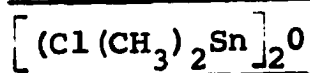
Dimethyltin chloride p-chlorobenzoate : $(\text{p-ClC}_6\text{H}_4\text{COO})\text{SnCl}(\text{CH}_3)_2$

Reaction 1: A solution of 0.22 g (0.001 mole) dimethyltin dichloride in 6 ml benzene was added to a solution of 0.46 g (0.001 mole) dimethyltin bis (p-Chlorobenzoate) in 8 ml benzene. Refluxing for two hours and standing at room temperature overnight yielded 0.03 g colorless needles, m.p. 214-215°. (Found: Sn, 25.43. Calcd. for $(\text{p-ClC}_6\text{H}_4\text{COO})\text{Sn}(\text{CH}_3)_2$: Sn, 25.81%).

Dimethyltin chloride p-toluate : $(\text{p-CH}_3\text{C}_6\text{H}_4\text{COO})\text{SnCl}(\text{CH}_3)_2$

Reaction 1: A solution of 0.55 g (0.0025 mole) dimethyltin dichloride and 1.05 g (0.0025 mole) dimethyltin bis(p-toluate) in 17 ml benzene were refluxed for three hours, the solvent completely evaporated off, and the residue dissolved in ligroin-benzene (1:1, v/v). Cooling yielded 0.07 g of white needles with a complex melting point. The filtrate, on cooling, afforded 0.36 g of a white powder, m.p. 93-97°. (Found: Sn, 35.83; Calcd. for $(\text{p-CH}_3\text{C}_6\text{H}_4\text{COO})\text{SnCl}(\text{CH}_3)_2$: Sn, 37.16%). This reaction was repeated twice with only slight variation. Although an improved melting point was obtained in one instance (95-98°) the yield was insufficient for analysis. In addition, these results were not reproducible when the scale of the reaction was increased.

Preparation of tetramethyl 1,3-dichlorodistannoxane :



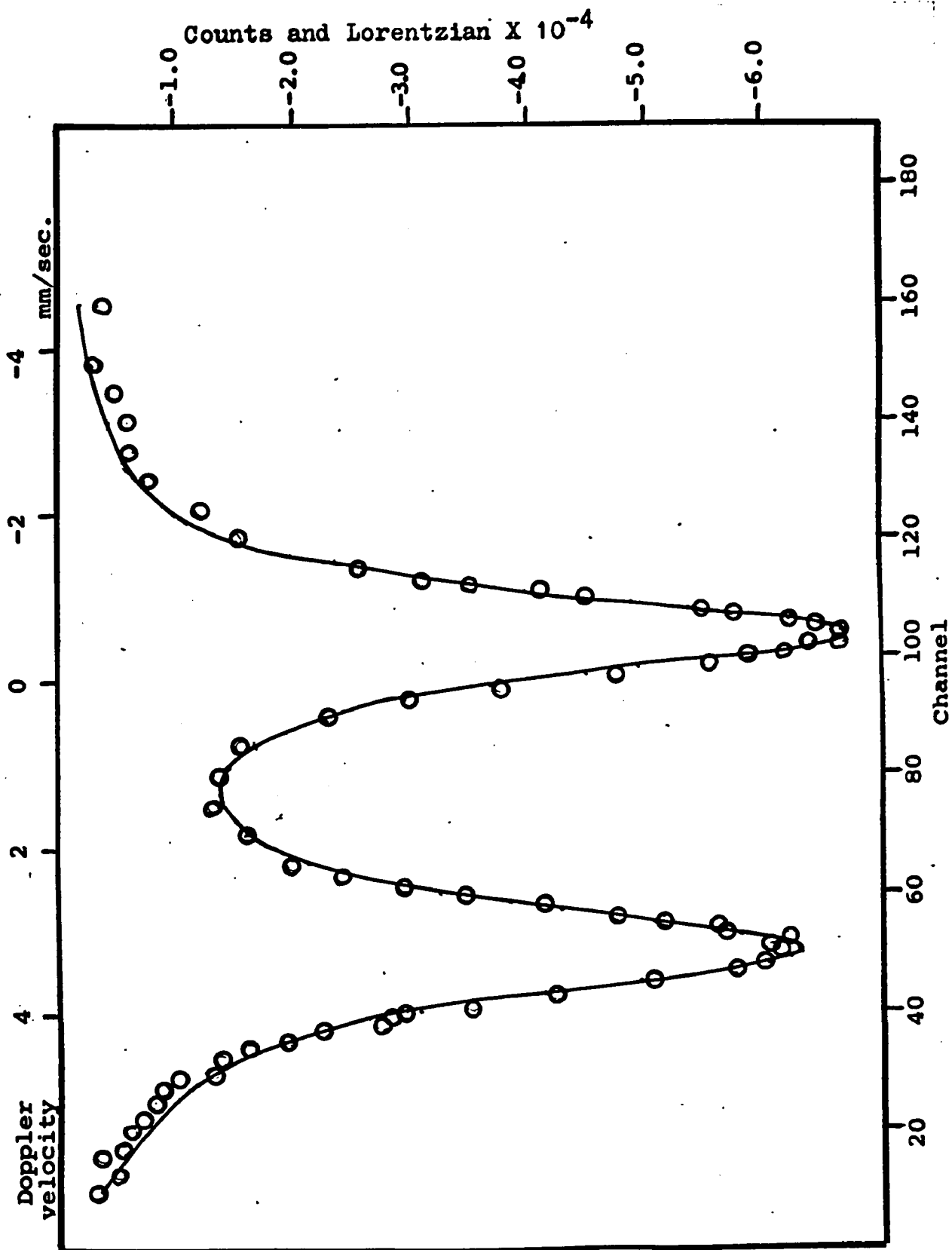
The method of Okawara and Wada¹⁷³ was used. A solution of 3.9 g (0.049 mole) pyridine in 30 ml ethanol (95%) was slowly added to a stirred solution of 11.0 g (0.050 mole) dimethyltin dichloride in 80 ml water. The reaction was stirred for an additional 30 min. The white precipitate was filtered, washed six times with ethanol (total volume of 75 ml), and air dried. This powder was dried overnight at 105° in a vacuum oven to yield 6.07 g, m.p. 318° (decomp.), lit¹⁷³ > 200°.

Reaction 3: The method of Wada, Shindo, and Okawara¹⁷⁵ was used with certain modifications as follows: A solution of 1.0 g (0.0026 mole) $\left[\text{Cl}(\text{CH}_3)_2\text{Sn} \right]_2\text{O}$, 0.71 g (0.0052 mole) p-toluic acid, and 2.04 g anhydron in 50 ml benzene was refluxed for 2 hours with stirring. This was filtered hot, condensed to a volume of 15 ml, and cooled to yield 0.13 g, m.p. 258° (decomp.) (Found: Sn, 43.23. Calcd. for (p-CH₃C₆H₄COO)SnCl(CH₃)₂: Sn, 37.16%; Calcd. for $\left[\text{Cl}(\text{CH}_3)_2\text{Sn} \right]_2\text{O}$: Sn, 61.75%; Calcd. for (p-CH₃C₆H₄COO) $\left[\text{Cl}(\text{CH}_3)_2\text{Sn} \right]_2$: Sn, 47.14%).

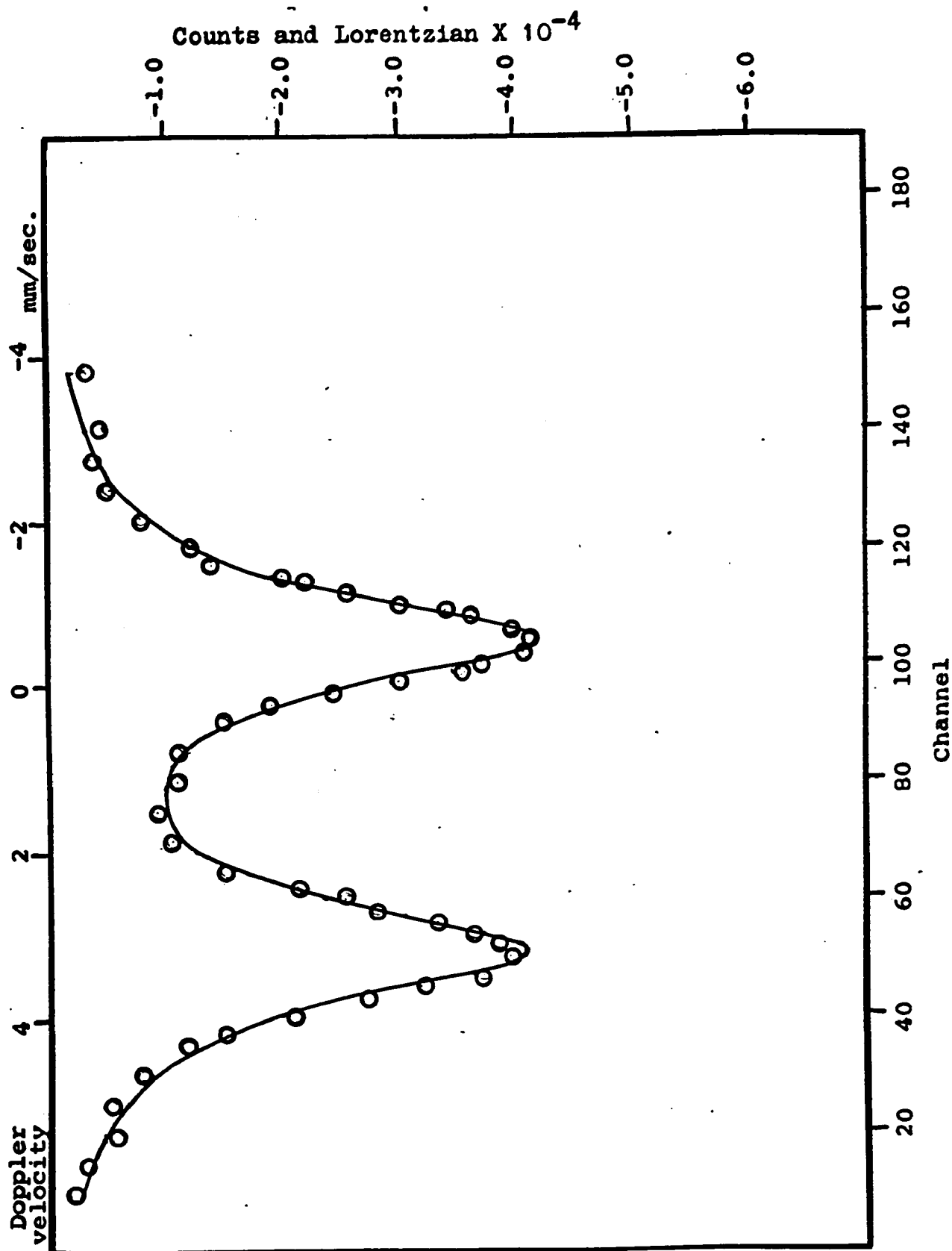
Dimethyltin chloride (p-methoxybenzoate) :



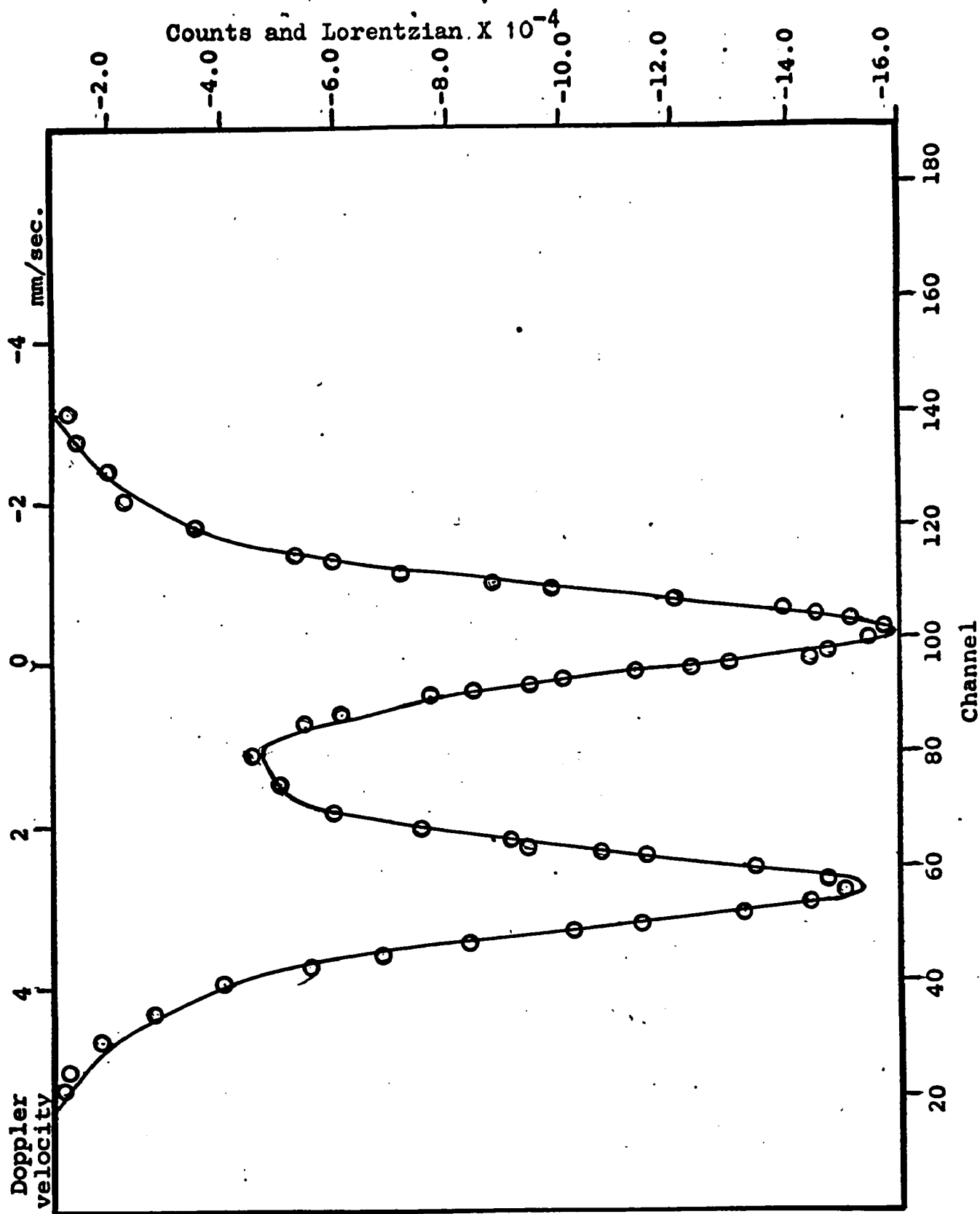
Reaction 1: A solution of 1.13 g (0.0025 mole) dimethyltin bis (p-methoxybenzoate) in 8 ml chlorobenzene was added to a solution of 0.55 g (0.0025 mole) dimethyltin dichloride in 6 ml chlorobenzene. Since no crystals formed on cooling, this solution was evaporated to dryness and the residue taken up in benzene-ligroin (1:1, v/v). Removal of some of the solvent and cooling yielded 0.66 g square plates, m.p. 154-164°. The NMR spectrum of this product corresponded to dimethyltin bis (p-methoxybenzoate), m.p. 171-173° (see Table XII). Three other runs were made with only slight variation in solvents or techniques. One yielded a product with m.p. 132-142° (not investigated further) while the other two attempts yielded p-methoxybenzoic acid as indicated by the m.p. and NMR spectra of the products.



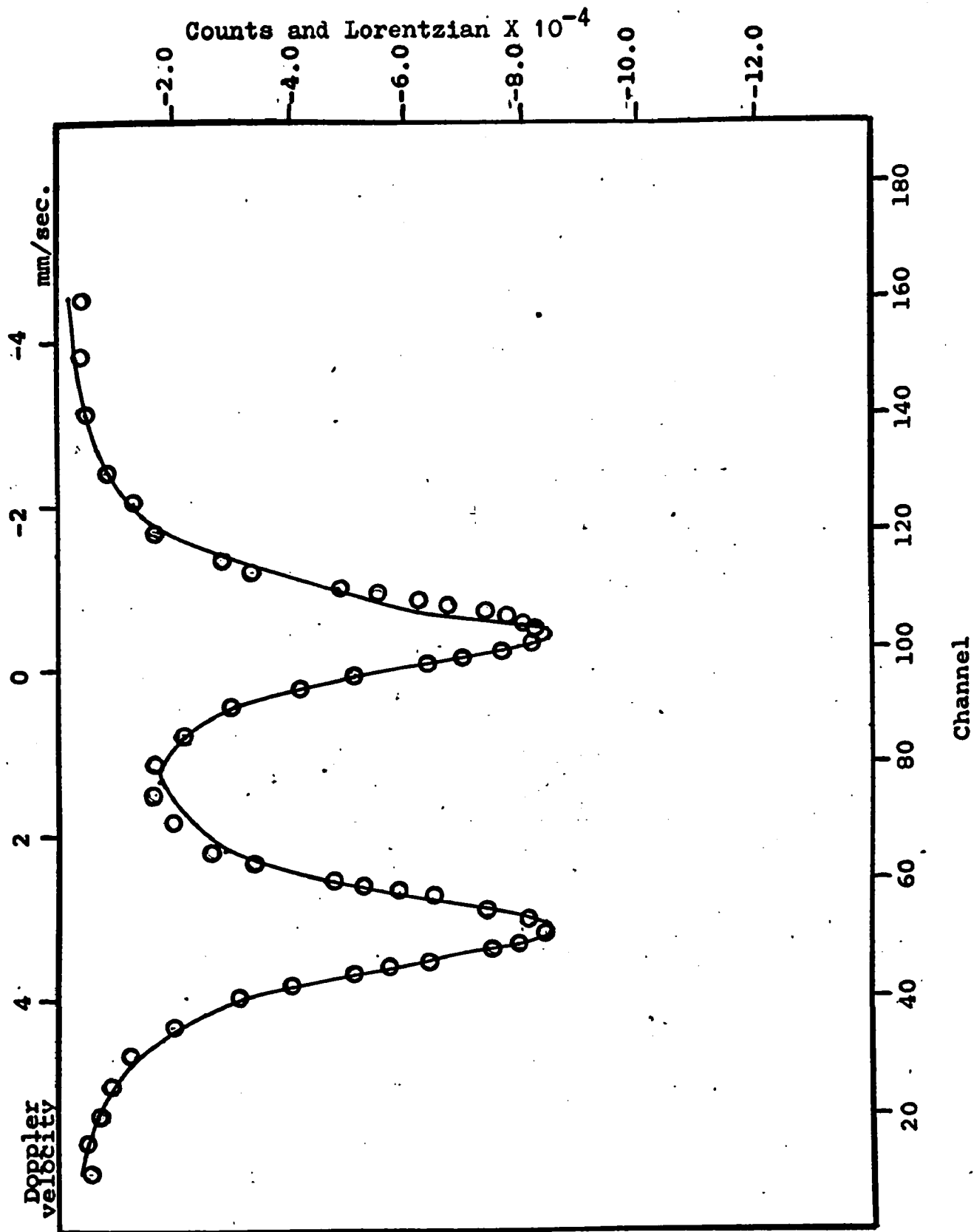
Appendix 1. Mössbauer spectrum of $(\text{C}_6\text{H}_5\text{COO})_2\text{Sn}(\text{CH}_3)_2$
at 77° K.



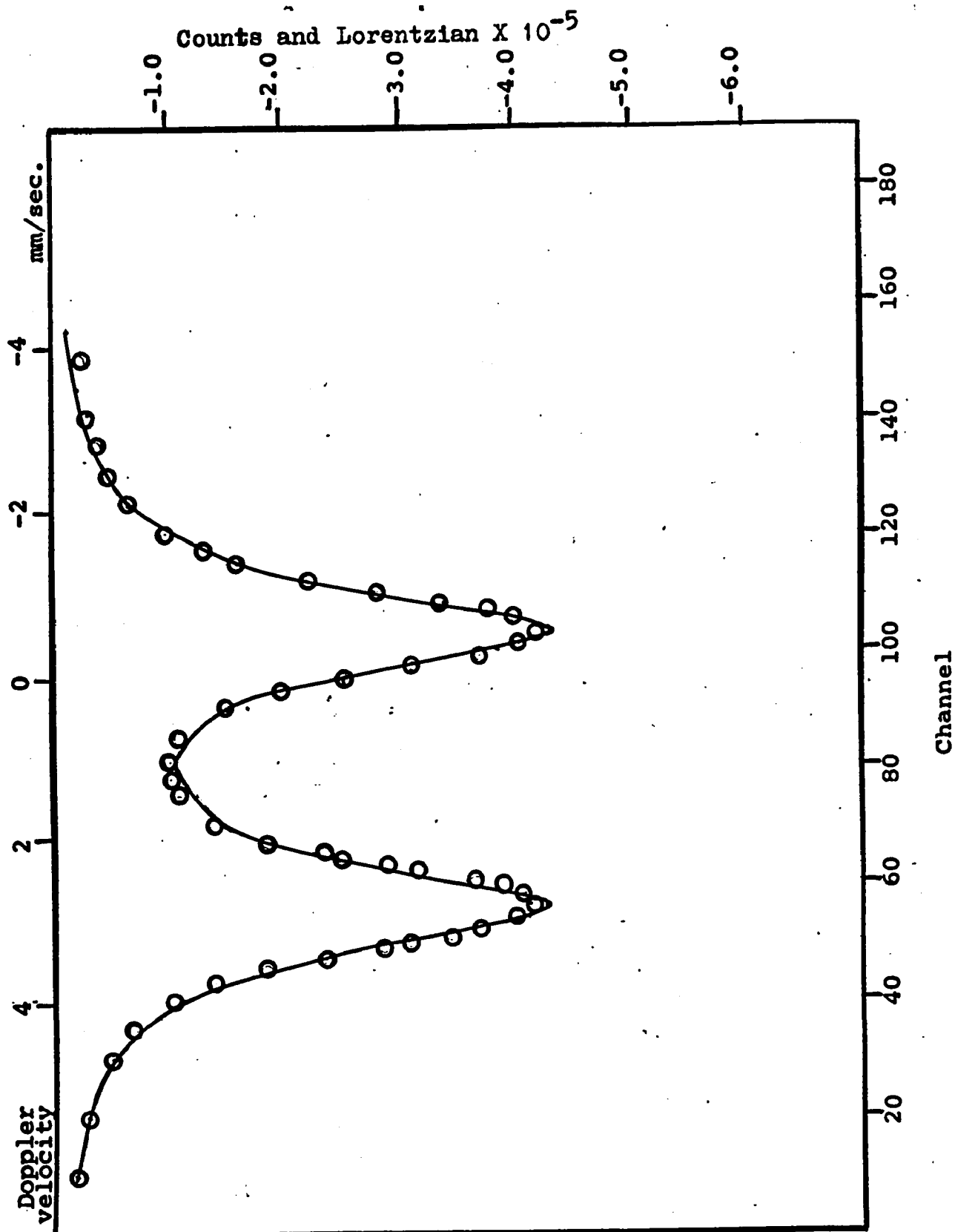
Appendix 2. Mössbauer spectrum of $(p\text{-ClC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$
at 77° K.



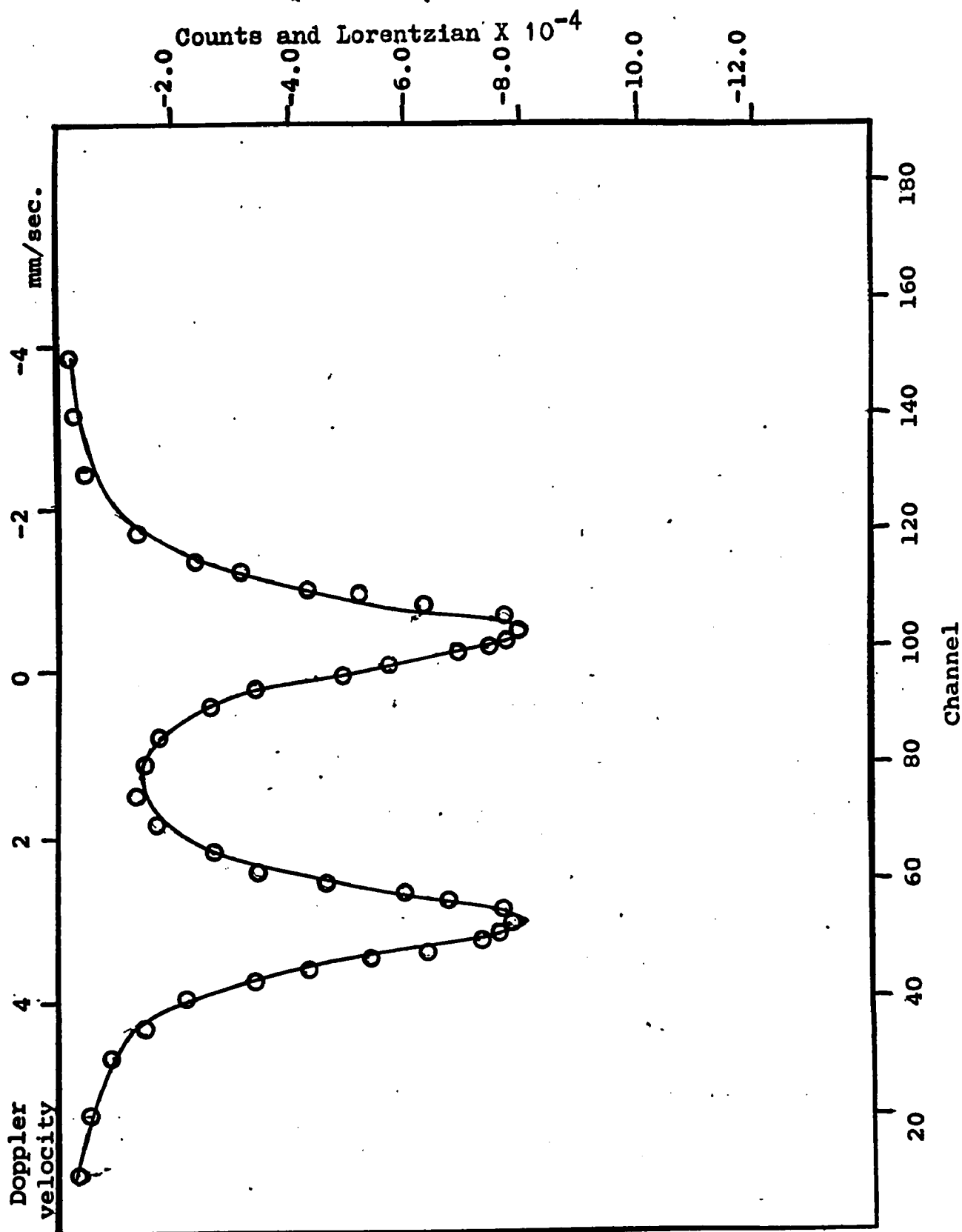
Appendix 3. Mössbauer spectrum of $(p\text{-NH}_2\text{C}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$
at 77° K.



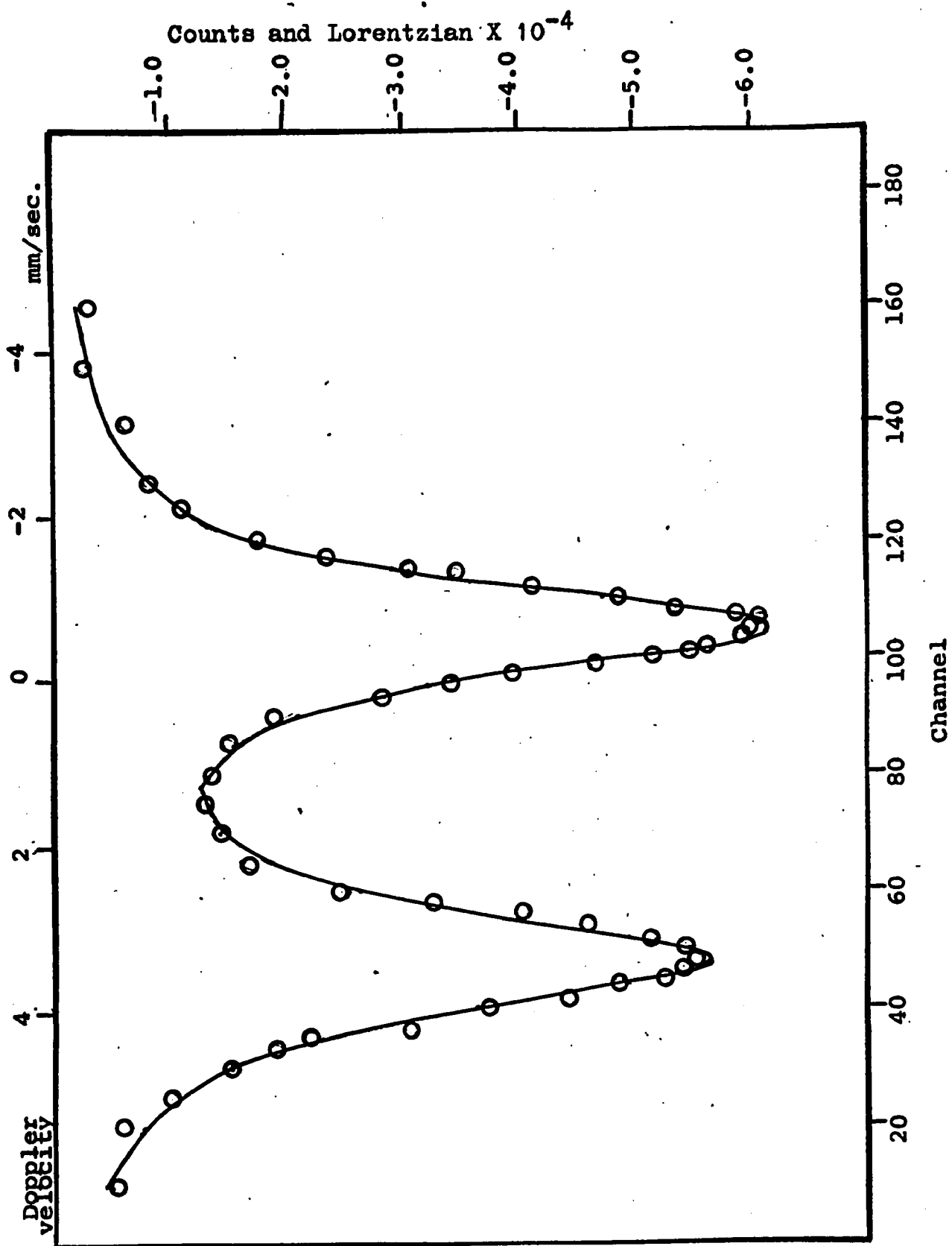
Appendix 4. Mössbauer spectrum of $(p\text{-NO}_2\text{C}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$
at 77° K.



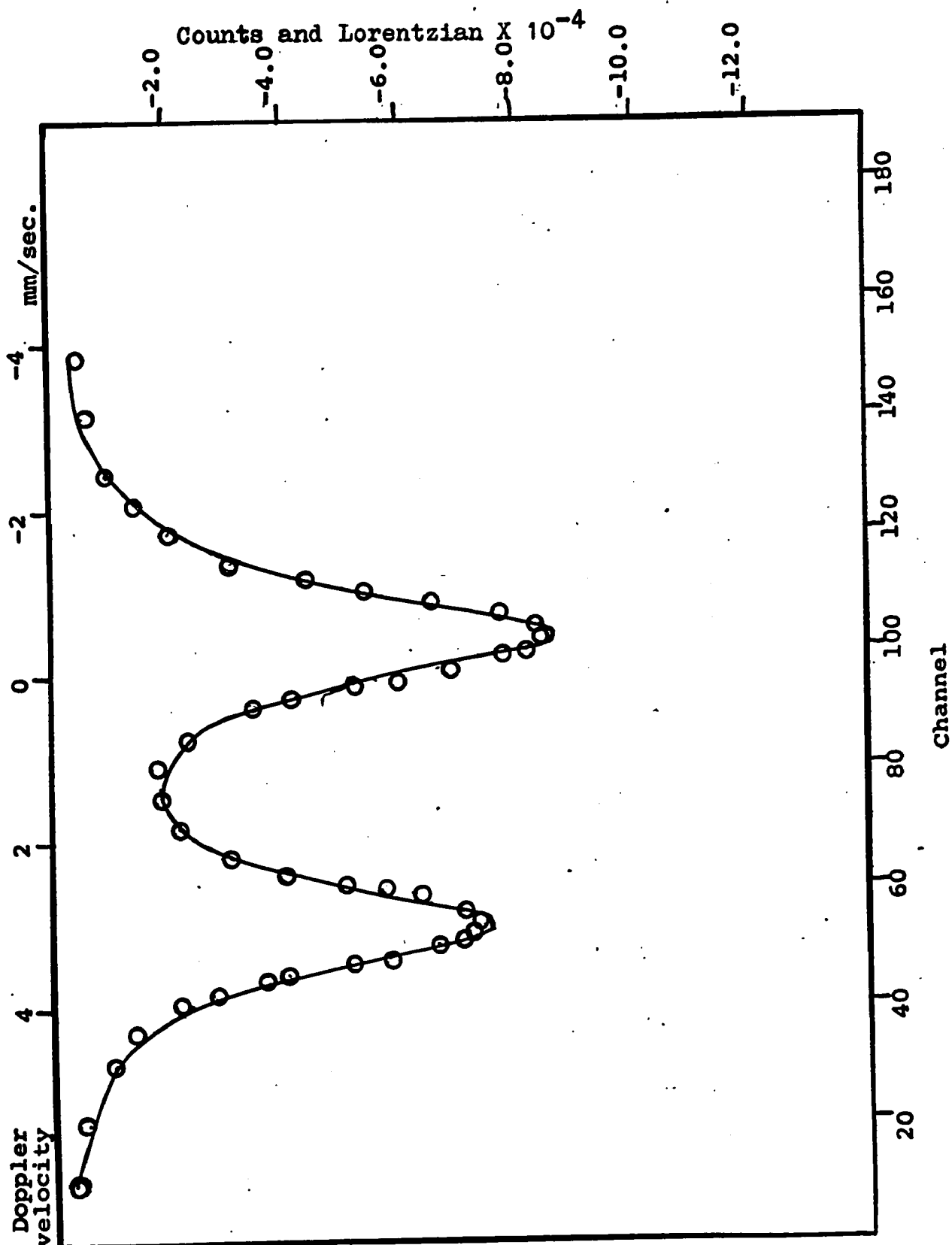
Appendix 5. Mössbauer spectrum of $(p\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ at 77°K .



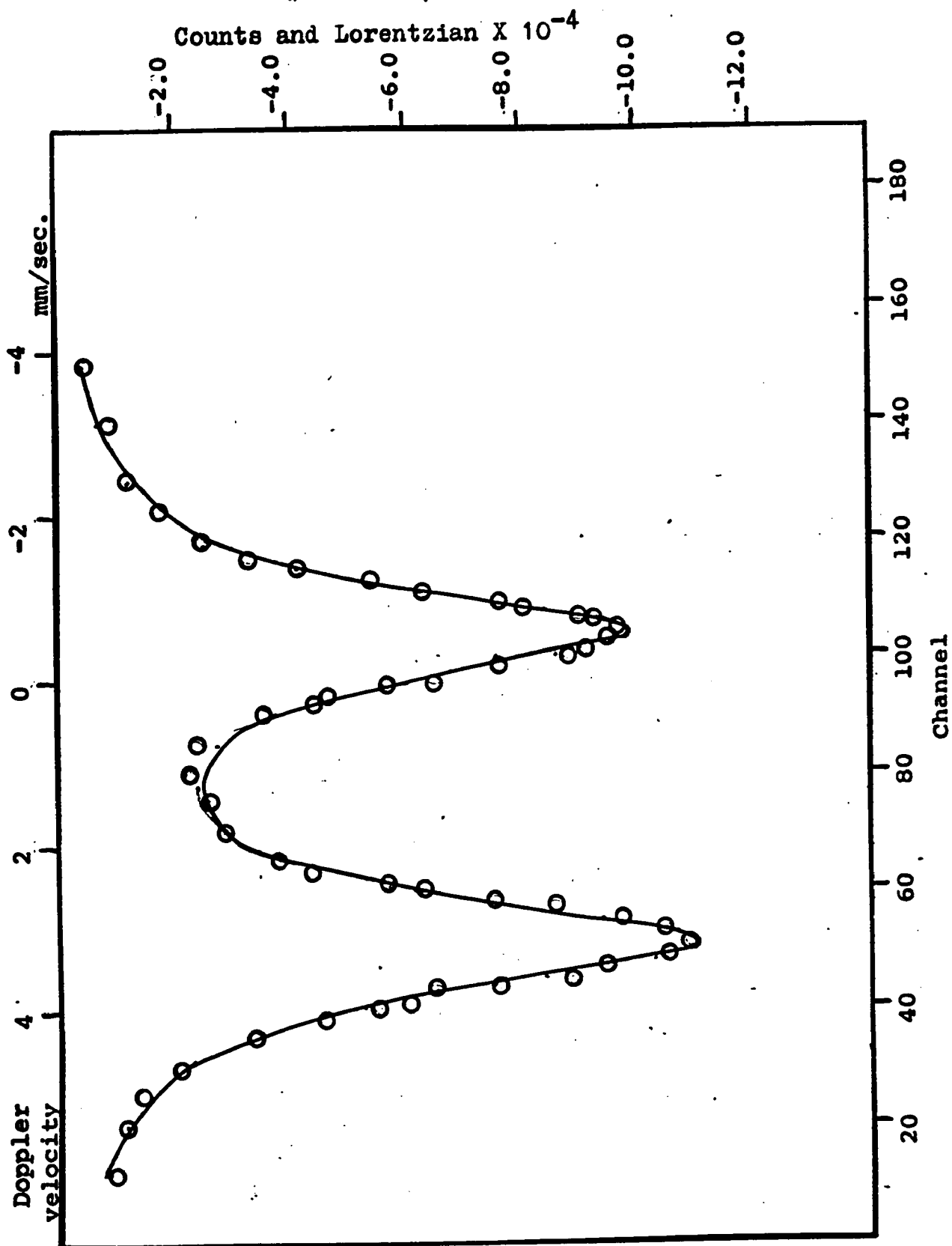
Appendix 6. Mössbauer spectrum of $(p\text{-CH}_3\text{OC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$
at 77° K.



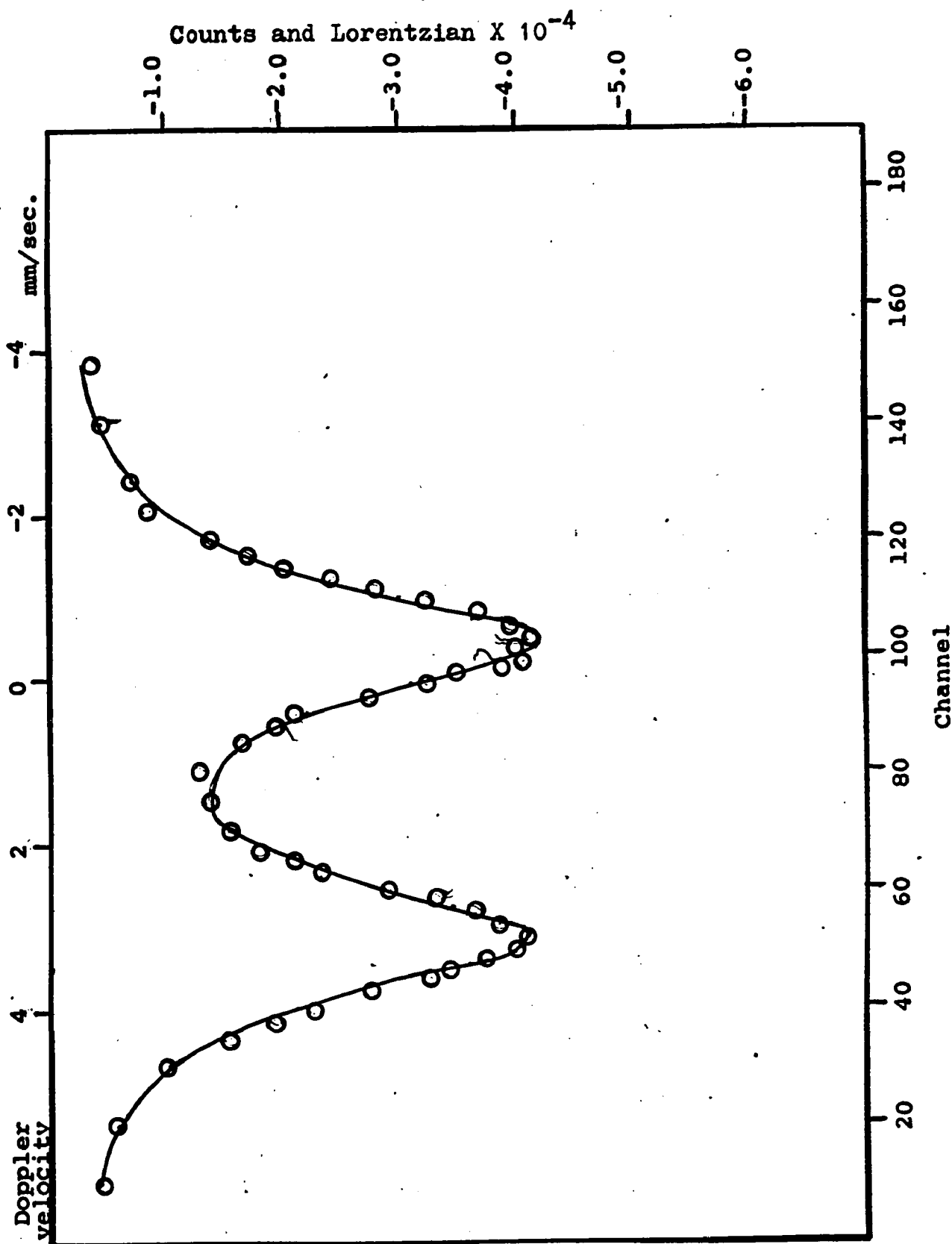
Appendix 7. Mössbauer spectrum of $(p\text{-CNC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$ at 77° K.



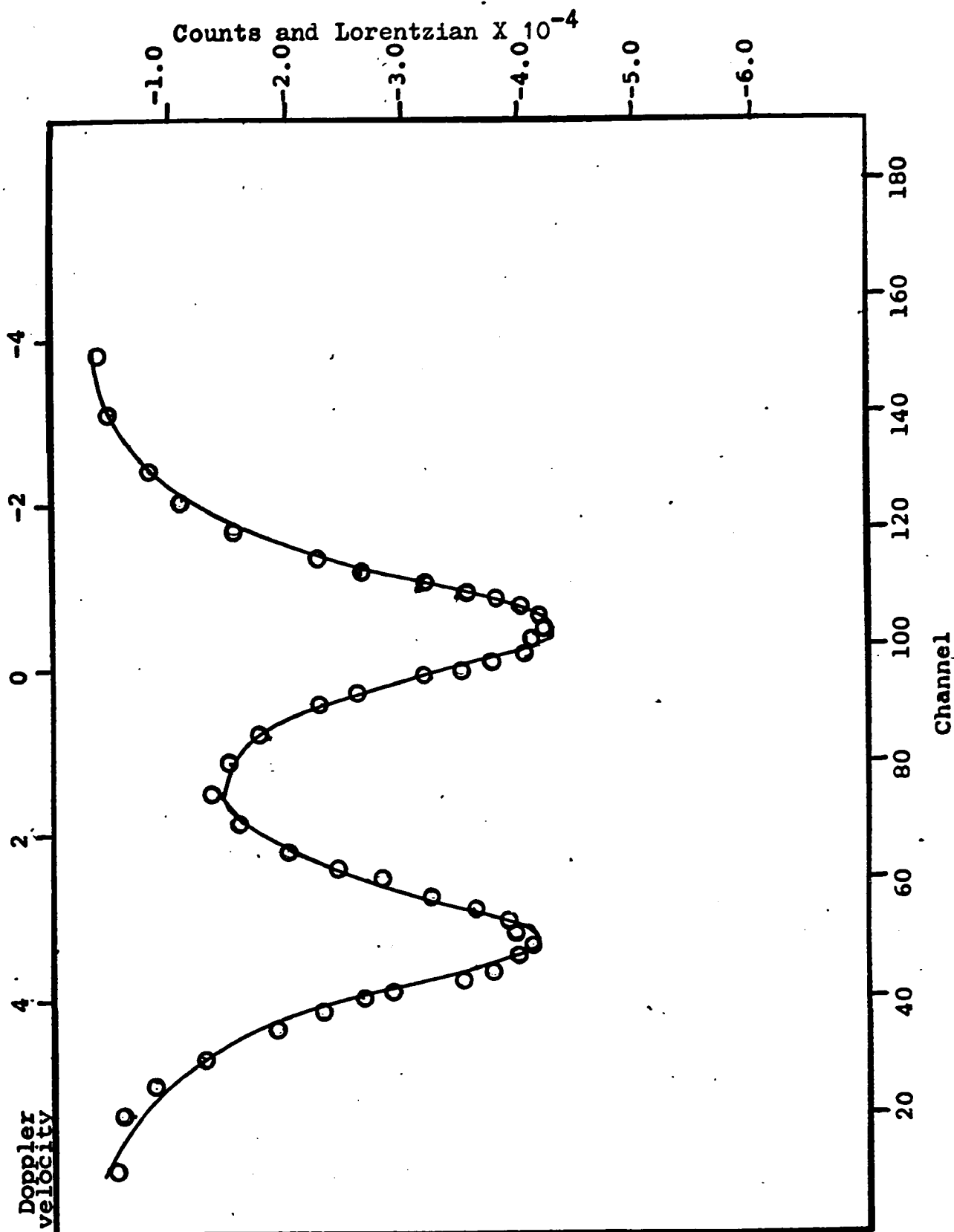
Appendix 8. Mössbauer spectrum of $(o\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$
at 77° K.



Appendix 9. Mössbauer spectrum of $(\text{CH}_3)_2\text{Sn}(\text{OOCCH}_2\text{Cl})_2$
at 77°K .



Appendix 10. Mössbauer spectrum of $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_3)$
at 77°K .



Appendix 11. Mössbauer spectrum of $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$
at 77° K.

APPENDIX 11-a

Mössbauer Parameters for $(p-XC_6H_4COO)_2Sn(CH_3)_2$ at

Room Temperature^a

X	ΔE	δ^b	Experimental Error ^c
H	3.49	1.21	± 0.09
NO ₂	3.39	1.27	± 0.03
Cl	3.23	1.15	± 0.07
NH ₂	2.87	1.02	± 0.11

^aData in mm/sec. ^bWith respect to BaSnO₃ as source.

^cCompounds with X = CN, CH₃, CH₃O were run with respect to Pd₃Sn as source at room temperature. Since the peaks were very broad and not too deep, it was difficult to determine the exact position of the peaks.

List of Abbreviations Used in Appendixes 12 - 22

<u>Assignment</u>	<u>Abbreviation</u>
C-H stretchings	ν (CH)
C-C stretchings	ν (CC)
In-plane C-H deformations	β (CH)
Out-of-plane C-H deformations	γ (CH)
Out-of-plane ring deformations	δ (CC)
In-plane ring deformations	α (CCC)
X-sensitive vibrations	X-sens.
Ring frequencies	ring

w, weak

s, strong

v, very

m, medium

sh, shoulder

br, broad

asym., asymmetric

sym., symmetric

deform., deformation

str., stretch

APPENDIX 12

Infrared Spectra of $(C_6H_5CO_2)_2Sn(CH_3)_2$

KBr	Nujol	CHCl ₃	C ₆ H ₆	C ₆ H ₅ COONa	Assignments
3070w					
3040 w, sh, br					
2929 w					
1979 vw					
1921 vw					
1830 vw					
1788 vw					
1766 vw					
1691 vw, br					
1620 w, sh	1621 vw, sh			1623 w, sh	
1602 s	1604 m	1608 s		1597 vs	v(CC)
	1591 vw, sh				
		1568 s			
1560 s	1563 m	1560 s, sh		1560 s, sh	} asym. CO ₂ ·str.
1547 s	1543 m	1545 m, sh		1547 vs	
1522 w, sh				1525 m, sh	

APPENDIX 12 (continued)

Infrared Spectra of $(C_6H_5CO_2)_2Sn(CH_3)_2$

KBr	Nujol	CHCl ₃	C ₆ H ₆	C ₆ H ₅ COONa	Assignments
1510 w, sh	1512 w, sh	1510 w, sh		1507 w, sh	∅ semicircle str.
1492 w	1495 w	1493 w		1495 w, sh	ν (CC)
	1458 w, sh	1479 w, sh			
1450 m	1450 m	1450 m			
	1439 w, sh			1438 w, sh	∅ semicircle str.
1415 s, sh					
1406 s, sh					
1396 s, sh, br	1397 m, sh				
1371 vs	1375 s, br	1366 vs, sh		1407 vs	} sym. CO ₂ str.
		1358 vs			
1318 w	1317 vw, sh				
1302 w	1302 vw	1305 w		1303 w	ν (CC)
1280 w, sh, br					
1256 vw, sh, br					

APPENDIX 12 (continued)

Infrared Spectra of $(C_6H_5CO_2)_2Sn(CH_3)_2$

KBr	Nujol	CHCl ₃	C ₆ H ₆	C ₆ H ₅ COONa	Assignments
1224 vw					sym. CH ₃ deform.
1217 vw, br					
1197 vvw					
1172 w	1180 vw	1184 w			
1159 vw, sh	1166 vw				
1129 w	1135 vw	1129w			
1095 vvw, sh					
1065 w	1075 vw	1076 vw		1071 w	β (CH)
1019 w	1026 vw	1031 w		1030 w	β (CH)
939 vw	941 vvw				
930 vw, br				921 w	γ (CH)
907 vw, sh, br					
859 w	865 vw			847 m	X-sens.
842 w, sh	850 vw, sh			821 w	γ (CH)
785 m	791 vw				CH ₃ rock
	730 w, sh				

APPENDIX 12 (continued)
Infrared Spectra of $(C_6H_5CO_2)_2Sn(CH_3)_2$

KBr	Nujol	CHCl ₃	C ₆ H ₆	C ₆ H ₅ COONa	Assignments
710 s	720 m			710 s	ø (CC)
680 m	686 w			701 s, sh	
660 w, sh				682 s	CO ₂ sym. deform.
645 vw, br					
589 vw	576 vvw	572 vw	572 vw		asym. SnC ₂ str.
539 vw, sh		553 w, sh, br	556 vw, sh, br		sym. SnC ₂ str.
530 vw	528 vvw	526 vw	530 vw	520 w	CO ₂ rock
500 vw	512 vvw, sh	508 vw, br	506 vvw, br		
469 vw, sh					
460 w, sh		455 w, br	452 w		
443 w					
434 w, sh	436 vw				Sn-O str.
420 w		423 vw		417 w, sh	X-sens.
				387 w	ø (CC)

APPENDIX 13

Infrared Spectra of $\underline{\text{p-ClC}_6\text{H}_4\text{CO}_2}_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl_3	C_6H_6	$\underline{\text{p-ClC}_6\text{H}_4\text{COONa}}$	Assignments
3093 w					
3076 w					
3056 w					
2978 w,br					
2818 w,br					
2678 w,br					
2548 w,br					
1926 vw,br					
1796 vw,br					
		1704 vw,br			
1689 w,br					
	1656 vw				
1621 w,sh					
	1597 vw,sh				
1594 s	1570 s	1596 s		1592 m	$\nu(\text{CC})$
1561 w,sh	1557 w,sh				
1544 m,br	1537 m	1555 m,br		1537 m	asym. CO_2 str.

APPENDIX 13 (continued)

Infrared Spectra of $\underline{\text{p-ClC}_6\text{H}_4\text{CO}_2}_2\text{Sn(CH}_3)_2$

KBr	Nujol	CHCl ₃	C ₆ H ₆	$\underline{\text{p-ClC}_6\text{H}_4\text{CO}_2\text{Na}}$	Assignments
	1528 m				
1510 vw, sh	1510 m	1523 m, sh			
	1501 m, sh	1509 m, sh			
1487 vw	1483 w, sh	1488 w			
1459 vw	1461 m, sh				
	1440 m				
	1432 m				
1424 w, sh	1424 m, sh				
1406 s	1384 s	1399 s		1407 m	
		1361 s, sh			
1372 m	1349 s	1349 vs		1394 m	sym. CO ₂ str.
1326 w, sh, br	1314 w, sh, br	1311 w, sh			
1306 vw					
1291 vw	1280 w	1291 w			
1277 vw	1265 w	1277 w			
	1253 w				
1228 vw	1212 vw				
1196 vvw, sh, br					

APPENDIX 13 (continued)

Infrared Spectra of $(\underline{p}\text{-ClC}_6\text{H}_4\text{CO}_2)_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl_3	C_6H_6	$\text{p-ClC}_6\text{H}_4\text{COONa}$	Assignments
1165 vw	1173 vw	1175 w			
	1155 vw, sh				
	1146 w	1138 w			
1126 vw	1114 vw				
1103 vw, sh					
1085 w	1083 vw, sh	1092 m		1094 w, br	$\nu(\text{C-Cl})$
1060 vvw, sh	1069 m				
1027 vw, sh		1021 w			
1008 w	999 w, sh				
	990 w				
966 vvw, sh					
948 vvw, sh					
921 vw, br					
859 w	843 w			849 w	$\gamma(\text{CH})$
846 w	831 w				
794 w	779 vw			774 w	$\delta(\text{CC})$
761 m	746 s				
726 vw, br	709 vw				

APPENDIX 13 (continued)

Infrared Spectra of $\underline{\text{p-ClC}_6\text{H}_4\text{CO}_2}_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl_3	C_6H_6	$\underline{\text{p-ClC}_6\text{H}_4\text{COONa}}$	Assignments
676 vw	663 vw				
655 vw, sh, br					
632 vw					
	612 vw				
590 vw, sh					
570 w	574 vw	568 m	578 m		asym. SnC_2 str.
	551 m			531 vw	
530 w			529 w		sym. SnC_2 str.
	520 vw, sh	519 w			
	510 w				
500 vw		498 vw, sh	502 vw, sh		
480 vw	481 vw	472 vw	482 vw		
	461 vw				
390 vw	370 w	383 vw, br	392 vw		Sn-O str.
350 vvw, sh, br					
320 vvw					

APPENDIX 14

Infrared Spectra of $(\underline{\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl ₃	C ₆ H ₆	p-CH ₃ C ₆ H ₄ COONa	Assignments
3075 w, sh					
3043 w				3030 m	ν(CH) phenyl
2985 w, br					
2920 w				2924 m	ν(CH) methyl
2870 w, sh					
2830 w, sh, br					
2650 w, br	2640 w, br				
2545 w, br	2520 w, br				
1927 vw, br					
1805 vw, br					
1740 w, sh					
1725 w, sh					
1706 m, sh					
1694 s, sh	1688 m, sh			1690 vw, br	
1679 s	1676 s				
1662 m, sh	1667 m, sh				
	1658 m, sh				
	1648 m, sh				
1627 s	1626 m				

APPENDIX 14 (continued)

Infrared Spectra of $\underline{\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2}_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl ₃	C ₆ H ₆	$\underline{\text{p-CH}_3\text{C}_6\text{H}_4\text{COONa}}$	Assignments
1616 s	1612 m				
1596 s	1593 m	1600 vs		1592 vs	$\nu(\text{CC})$
1577 m	1573 m			1563 s, sh	
1547 s, sh		1558 s		1550 vs	asym. CO ₂ str.
1543 s	1543 m, sh	1541 s, sh			
	1534 m	1534 m, sh			
1523 m, sh					
1516 s, sh	1518 m, sh				
	1508 m, sh	1506 m		1490 m	
1458 w	1452 m			1449 m	
1418 s, sh		1401 s			
1402 vs	1398 s	1351 vs, br		1416 vs, br	sym. CO ₂ str.
1386 s, sh	1375 m			1383 s	sym. CH ₃ deform.
1359 s, sh					
1328 s	1329 s				
		1313 m, sh			
1296 m, sh	1294 m, sh	1300 w			
1283 s	1282 m	1289 w		1287 w	

APPENDIX 14 (continued)

Infrared Spectra of $(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2)_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl_3	C_6H_6	$\underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{COONa}$	Assignments
1239 m					
1216 w				1206 w	
1197 w, sh					
1191 m, sh	1186 w, sh				
1182 s	1177 m	1181 m		1183 w	β (CH)
1134 w	1132 w	1137 m		1149 m	
1120 w	1116 w	1120 w		1114 s	β (CH)
1105 vw		1100 vw, sh		1098 m	
1044 vw					
1023 w	1021 w	1022 w		1024 m	
963 w					
953 w, br	956 w, br				
872 vw, sh					
856 w, sh	851 w, sh			855 m	γ (CH)
841 w	836 w				
788 s	786 w			781 w, sh	
766 s	762 m, sh			761 vs	ϕ (CC)
	755 m				

APPENDIX 14 (continued)

Infrared Spectra of $\underline{\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2}_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl_3	C_6H_6	$\underline{\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2\text{Na}}$	Assignments
				696 m	
				690 m, sh	
646 m	648 w	654 w	648vw, sh, br		
		630 m	627 w		
617 m	615 w				
601 w	608 w, sh				
576 w	574 w	569 vw	569 vw		asym. SnC_2 str.
546 w	543 w	541 vw	544 vw		
523 m	522 w	521 vw	523 vw		sym. SnC_2 str.
506 m	507 m				
			498 vvw		
		472 w	473 vw		
466 w	465 w	464 vw, sh	463 vw, sh		
403 w		425 w	428 w		Sn-O str.
			398 vw, sh		
366 vw	378 m, br				

APPENDIX 15

Infrared Spectra of $\underline{\text{p-CH}_3\text{OC}_6\text{H}_4\text{COO}}_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl_3	$\underline{\text{p-CH}_3\text{OC}_6\text{H}_4\text{COO}}_2\text{Na}$	Assignments
3065 vw				
3048 vw				
3002 vw				
2960 w				
2938 w, br, sh				
2910 w, br, sh				
2827 w			2835 w	$\nu(\text{CH})$
1685 m				
1619 m, sh	1601 s, sh			
1594 vs	1593 s	1601 vs	1596 vs	$\nu(\text{CC})$
1563 m, sh	1573 w, sh		1560 s, sh	
	1558 m, sh			
1549 m, br	1543 m			} asym. CO_2 str.
1538 m, br	1536 m, sh	1559 s	1530 s, br	
		1543 m, sh		
1507 m	1503 m	1510 m		
	1487 w, sh	1488 w, sh	1498 s, sh	asym. CH_3 bend
1463 w, sh	1472 w, sh			

APPENDIX 15 (continued)

Infrared Spectra of $(\underline{p}\text{-CH}_3\text{OC}_6\text{H}_4\text{COO})_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl ₃	$\underline{p}\text{-CH}_3\text{OC}_6\text{H}_4\text{COONa}$	Assignments
1456 w	1454 m	1456 w		
	1442 m, sh			
1420 s	1415 s	1415 m		
1394 s, sh				
1383 s, sh				
1371 vs, br	1361 vs, br	1351 vs, br	1401 vs, br	sym. CO ₂ str.
1342 s, br, sh				
1295 s	1293 w	1309 m		
		1300 m, sh		
1248 vs	1254 s		1250 s	asym. COC str.
1192 m, sh	1187 w		1193 w, sh	
1172 s	1170 s	1172 s	1183 s	β (CH)
1147 vw	1144 w	1142 w	1148 w	
1130 vw				
1110 w	1105 w	1111 w	1102 m	β (CH)
1023 m	1021 m	1032 m	1038 s	sym. COC str.
922 vw				
872 w	870 vw	869 w		

APPENDIX 15 (continued)

Infrared Spectra of $\underline{\text{p-CH}_3\text{OC}_6\text{H}_4\text{COO}}_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl ₃	$\underline{\text{p-CH}_3\text{OC}_6\text{H}_4\text{COO}}_2\text{Na}$	Assignments
850 m	848 w		847 m	γ (CH)
	804 vw, br, sh			
782 s	780 s		778 s	ϕ (CC)
702 vw	696 vw		693 w	sym. CO ₂ deform.
663 m, sh		660 m, sh		
655 m	655 m	650 m, sh		
643 s	640 s	640 s	639 m	CO ₂ out-of-plane bend or COC bend
628 m	626 m	625 s	619 s	
		596 vw, sh		
579 w	578 vw	568 vw		Asym. SnC ₂ str.
541 w		549 vw	540 w	ϕ (CC)
529 w, sh		520 vw, sh		sym. SnC ₂ str.
501 w	505 vw	500 w	490 m, br	ϕ (CC)
494 w				
389 w	388 w	386 w		Sn-O str.

APPENDIX 16

Infrared Spectra of $\underline{\text{p-CNC}_6\text{H}_4\text{CO}_2}_2\text{Sn(CH}_3)_2$

KBr	Nujol	CHCl ₃	$\underline{\text{p-CNC}_6\text{H}_4\text{CO}_2\text{Na}}$	Assignments
3097 w				
3072 w			3077 vw	ν (CH)
3057 w, sh	3060 w, br			
2987 w, br			2915 vw	
2867 w, br				
2226 m	2225 w		2237 w	ν (CN)
1722 w, sh				
1707 m		1708 vw, br		
1642 w, sh		1640 w, sh	1658 w, sh	
1629 m, sh				
1621 m, sh				
1609 m, sh	1610 w, sh			
1596 s	1594 s	1604 s	1600 vs	ν (CC)
	1585 m, sh			
	1571 w, sh			
1564 w, sh	1560 w, sh			

APPENDIX 16 (continued)

Infrared Spectra of $(\underline{p}\text{-CNC}_6\text{H}_4\text{CO}_2)_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl ₃	$\underline{p}\text{-CNC}_6\text{H}_4\text{COONa}$	Assignments
1546 s, br	1546 m, sh	1551 m, br	1548 s	asym. CO ₂ str.
	1528 m	1521 m, sh		
1503 m	1506 m	1501 m		
	1488 w, sh			
1468 w, br				
	1458 m			
1421 s, sh				
1412 vs	1411 s	1409 s, sh		
1395 s, sh			1399 vs, br	} sym. CO ₂ str.
1381 s, sh	1376 s			
1366 s, sh		1348 vs, br		
	1339 w, sh			
1326 w, sh				
1302 w, sh	1304 w	1301 m		
1287 m	1286 w	1285 m	1294 w	
1182 w	1175 vw	1182 w		
1138 w	1135 vw	1133 w	1151 vw	
1116 w	1110 vw	1114 w, sh	1117 m	β (CH)

APPENDIX 16 (continued)

Infrared Spectra of $\underline{\text{p-CNC}_6\text{H}_4\text{CO}_2}_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	CHCl ₃	$\underline{\text{p-CNC}_6\text{H}_4\text{CO}_2\text{Na}}$	Assignments
1097 vw, sh	1089 vw	1098 vw, sh	1098 vw, sh	
1021 m	1016 vw	1022 w	1028 vw	β (CH)
873 m	870 w		869 w	
			852 w	γ (CH)
815 m, sh				
798 m, sh	800 w, br			
780 s	777 m		780 m	ϕ (CC)
769 m	764 m		765 w	
	694 w		693 w	sym.CO ₂ deform.
656 w		667 m		
642 w		643 w, sh	641 vw	
		597 m		
588 m	584 w	579 w, sh		asym. SnC ₂ str.
564 w, sh		562 w, sh	562 m	
	555 vw, sh			
547 m	542 w	546 m	543 m	ϕ (CC)
525 w	529 vw, sh	522 vw, sh		sym. SnC ₂ str.
500 w			500 vw	ϕ (CC)
404 w		400 w, br	396 w	
391 w	387 w, br	389 w		Sn-O str.

APPENDIX 17

Infrared Spectra of $(\underline{p}\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2)_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	$\underline{p}\text{-NO}_2\text{C}_6\text{H}_4\text{COONa}$	Assignments
3114 vw			
3050 vw, sh, br			
2985 vvw, br			
2853 vvw			
1951 vvw			
1813 vvw			
1723 vw, sh			
1711 w, sh			
1641 w, sh	1636 vw, sh		
1625 m	1620 w	1617 s	$\nu(\text{CC})$
1602 m, sh	1596 m, sh		
1583 s, br	1583 m	1584 vs	asym. CO_2 str.
1561 m, sh	1559 w, sh	1566 s, sh	
1522 s	1524 m	1517 s	asym. NO_2 str.
	1506 w, sh		
1490 vw, sh	1495 w, sh	1497 m, sh	
1459 vw, br	1451 w		
1441 vw, sh			
1411 s	1406 m	1402 vs	} sym. CO_2 str.
1363 m, sh	1364 m		
1344 vs	1342 s	1349 vs	sym. NO_2 str.
1321 m	1317 m	1317 m	$\nu(\text{CC})$
1274 w, sh, br			
1224 vw, br			sym. CH_3 deform.
1168 vw			

APPENDIX 17 (continued)

Infrared Spectra of $(p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2)_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	$p\text{-NO}_2\text{C}_6\text{H}_4\text{COONa}$	Assignments
1139 vw	1136 w		
1108 w	1105 w	1109 w	X-sens.
1087 vw, sh	1087 vw, sh		
1017 vw	1016 w	1021 vw	β (CH)
877 w	879 w	880 w	C-N str.
844 w, br	844 w	836 m	γ (CH)
799 m	797 w	804 m	X-sens.
772 vw, sh	763 vw, sh		CH_3 rock
722 m	723 m	727 s	ϕ (CC)
633 vw, br			
582 w, sh			
571 w	567 w		asym. SnC_2 str.
		557 vw	
528 w	523 vw		sym. SnC_2 str.
502 w	497 vw	506 m	ϕ (CC)
378 vw	369 w, br		Sn-O str.

APPENDIX 18

Infrared Spectra of $(\underline{p}\text{-NH}_2\text{C}_6\text{H}_4\text{CO}_2)_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	$\underline{p}\text{-NH}_2\text{C}_6\text{H}_4\text{COONa}$	Assignments
3464 m,br	3480 s		
3385 m,sh	3375 vw	3375 m	asym. NH_2 str.
3359 m			
3339 m,sh		3300 m	sym. NH_2 str.
3219 w	3236 m	3240 m,br,sh	
3039 vw,br			
2909 vw			
2659 vw	2668 w,br		
1907 vw,br			
1773 vw,br			
1676 vw,sh			
	1643 s,sh		
1634 m	1630 s		
1612 m,sh		1612 s,sh	NH_2 scissor
1601 s	1593 vs	1600 s	$\nu(\text{CC})$
1585 w,sh	1563 s,sh		
1545 m	1548 s	1530 s,br	asym. CO_2 str.
1506 w	1509 s	1510 s,sh	
	1495 m,sh		
1472 w,sh			
	1459 m,sh		
1433 w	1442 s		
	1398 m,sh	1410 s,sh	
1372 s,sh			
1360 s	1353 vs,br	1400 s,br	sym. CO_2 str.

APPENDIX 18 (continued)

Infrared Spectra of $(p\text{-NH}_2\text{C}_6\text{H}_4\text{CO}_2)_2\text{Sn}(\text{CH}_3)_2$

KBr	Nujol	$p\text{-NH}_2\text{C}_6\text{H}_4\text{COONa}$	Assignments
1332 m, sh	1338 s, sh		
1322 w	1321 s	1318 w, sh	ν (CC)
1294 w	1300 s		
1256 vw, sh, br		1260 m	CN str.
1217 vw, sh, br			sym. CH_3 deform.
1209 vw, sh, br	1211 w		
1175 m	1179 s	1180 w	β (CH)
1138 vw	1141 m	1121 vw	
1081 vw, sh, br	1080 w	1086 vw	
1008 vw		1018 vw	β (CH)
953 vw	956 w		
868 w, sh	870 w	876 w, sh	
844 w	844 m	838 m	γ (CH)
	806 w, sh, br		
783 m	785 s	781 s	ϕ (CC)
763 w, sh, br	759 w, sh		
700 w	706 w	691 w	sym. CO_2 deform.
654 m	650 s		
644 w, sh	641 m, sh	620 m	CO_2 out-of-plane bend
575 w	576 w		asym. SnC_2 str.
541 w, sh	551 w		
524 w	530 w	534 vw	sym. SnC_2 str.
501 w	500 w	490 w	ϕ (CC)
473 w, sh			
440 w	444 m		Sn-O str.
385 vw		370	

APPENDIX 19

Infrared Spectra of $(\text{CH}_3)_2\text{Sn}(\text{OOCCH}_2\text{Cl})_2$

KBr	CHCl_3	$\text{ClCH}_2\text{COONa}^a$	Assignment ^a
3010 vw			
2960 w			
2925 w			
1716 w, sh, br	1729 w		
1678 m			
1627 s, sh			
1611 s	1633 vs, br	1595	asym. CO_2 str.
	1607 s, sh		
1511 w, sh, br			
1406 s	1410 s	1399	CH_2 scissor
1376 bs, br	1361 vs	1425	sym. CO_2 str.
1347 s, sh			
1237 s		1248	CH_2 wag
		1166	CH_2 twist
	1036 vw		
954 vw, sh	949 vw, sh		
931 w	934 w	933	CH_2 rock
	920 w, sh	926	CC str.

APPENDIX 19 (continued)

Infrared Spectra of $(\text{CH}_3)_2\text{Sn}(\text{OOCCH}_2\text{Cl})_2$

KBr	CHCl_3	$\text{ClCH}_2\text{COONa}^a$	Assignment ^a
783 s		770	CCl str.
695 m, br			
669 m, sh		670	COO scissor
640 m			
588 m	580 w		asym. SnC_2 str.
533 w	525 w		sym. SnC_2 str.
507 m	504 w		
		429	COO rock
488 m, sh			
	364 vw		

^aReference 151.

APPENDIX 20

Infrared Spectra of $(C_6H_5)_2Sn(OOCC_6H_5)_2$

KBr	CHCl ₃	C ₆ H ₅ COONa	Assignments
3063 m			
3008 w, sh			
2993 w			
1692 w			
		1623 w, sh	
1601 s, sh	1605 s		
1596 vs		1597 vs	v(CC)
		1560 s, sh	
1546 vs, br	1567 s	1547 vs	asym. CO ₂ str.
1534 vs, br			
1520 vs, br			
		1525 m, sh	
1497 s	1493 w	1507 w, sh	∅ semicircle str.
1483 s	1482 w	1495 w, sh	v(CC)
1450 vs	1450 m		
	1442 m	1438 w, sh	∅ semicircle str.
1392 vs, br	1361 vs	1407 vs	sym. CO ₂ str.
1320 m			

APPENDIX 20 (continued)

Infrared Spectra of $(C_6H_5)_2Sn(OOCC_6H_5)_2$

KBr	CHCl ₃	C ₆ H ₅ COONa	Assignments
1307 m	1305 m	1303 w	ν (CC)
1289 w, sh			
1261 w			
1194 w, sh			
1178 m			
1164 w			
1139 w	1133 w		
1071 m	1070 w	1071 w	β (CH)
1025 m	1024 w	1030 w	β (CH)
1000 m	999 w		
945 vw, sh			
937 vw	923 vw	921 w	γ (CH)
910 vw			
872 m			
863 s	865 w	847 m	X-sens.
818 vw		821 w	γ (CH)
727 vs, sh			
717 vs		710 s	δ (CC)

APPENDIX 20 (continued)

Infrared Spectra of $(C_6H_5)_2Sn(OOCC_6H_5)_2$

KBr	$CHCl_3$	C_6H_5COONa	Assignments
		701 s, sh	
688 vs		682 s	sym. CO_2 deform.
	620 w		
591 vw	590 vw		
	567 vw		
550 w	545 vw		
531 w	521 vw	520 w	CO_2 rock
	495 vw		
	455 w		
448 vs	444 m		
		417 w, sh	X-sens.
		387 w	ϕ (CC)
340 vw	361 m		

APPENDIX 21

Infrared Spectra of $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$

KBr	CHCl_3	$\text{ClCH}_2\text{COONa}^a$	Assignment ^a
2990 vw			
2945 vw			
2920 vw, sh			
	1727 w		
1716 vw, sh			
1664 vw, sh			
1583 vs, br	1632 s	1595	asym. CO_2 str.
1561 s, sh	1597 m, sh		
1546 s, sh			
1510 m, sh			
	1408 s		
1397 s, br	1371 s	1425	sym. CO_2 str.
1348 w, sh			
1248 s		1248	CH_2 wag
1230 w, sh			
	1035 vw		
937 vw	947 vw, sh	933	CH_2 rock

APPENDIX 21 (continued)

Infrared Spectra of $(\text{CH}_3)_2\text{SnCl}(\text{OOCCH}_2\text{Cl})$

KBr	CHCl_3	$\text{ClCH}_2\text{COONa}^a$	Assignment ^a
	929 vw, sh	926	CC str.
817 m, sh			
789 s		770	CCl str.
678 w		670	COO scissor
638 vw			
	619 w		
578 w	565 w		asym. SnC_2 str.
568 w, sh, br			
524 w, sh	523 w		sym. SnC_2 str.
504 m	497 vw		
	360 m		
	342 m, br		
330 m ^b			SnCl str.

^aReference 151.

^bNujol mull between CsBr plates.

APPENDIX 22

Infrared Spectra of $(C_6H_5)_2SnCl(OOCC_6H_5)$

KBr	CHCl ₃	C ₆ H ₅ COONa	Assignments
3073 w			
3053 w			
3013 vw, sh			
2995 vw			
1692 w	1700 vw		
		1623 w, sh	
1598 s	1601 m	1597 vs	ν (CC)
		1560 s, sh	
1547 s	1547 s	1547 vs	asym. CO ₂ str.
		1525 m, sh	
		1507 w, sh	∅ semicircle str.
1495 w	1493 w	1495 w, sh	ν (CC)
1481 m	1481 m		
1450 m	1451 m		
		1438 w, sh	∅ semicircle str.
1432 s	1432 m		
1398 s, sh, br	1401 s, sh		
1377 s	1388 s, br	1407 vs	sym. CO ₂ str.

APPENDIX 22 (continued)

Infrared Spectra of $(C_6H_5)_2SnCl(OOCC_6H_5)$

KBr	$CHCl_3$	C_6H_5COONa	Assignments
1334 w	1332 w		
1317 w			
1308 w	1306 w	1303 w	ν (CC)
1290 w, sh			
1193 vw			
1176 w			
1159 vw			
1137 w	1138 w		
	1093 vw		
1070 m	1073 w	1071 w	β (CH)
1024 w	1024 w	1030 w	β (CH)
997 w	1000 w		
		921 w	γ (CH)
875 w	878 w		
		847 m	X-sens.
		821 w	γ (CH)
728 s, sh			
718 vs		710 s	ϕ (CC)
		701 s, sh	

APPENDIX 22 (continued)

Infrared Spectra of $(C_6H_5)_2SnCl(OOCC_6H_5)$

KBr	CHCl ₃	C ₆ H ₅ COONa	Assignments
689		682 s	sym. CO ₂ deform.
	624 w		
597 vw	593 vw		
	567 vw		
549 vw	544 vw		
	523 vw	520 w	CO ₂ rock
	496 w		
466 w	464 w		
446 m	447 m		
	404 w, sh	417 w, sh	X-sens.
	385 w		
	363 m		
340 vw			
317 m ^a			Sn-Cl str.

^aNujol mull between CsBr plates.

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