## Discussion

Previous investigations of astatine chemistry have shown that its behavior is not too different from that of other halogens.[3,5,6] These studies have characterized a "zero oxidation state" of astatine that is volatile, is soluble in organic solvents, and has a tendency to adsorb on surfaces. Unfortunately, another characteristic of this state has been severe irreproducibility of behavior. Much the same situation is found with very small amounts of iodine,[7–11] and it seems reasonable to attribute the difficulties to the fact that some or all of the halogen is tied up in the form of compounds with organic impurities.[6,7,11] On the other hand, when "zero-state" astatine is mixed with other halogens, it is often possible to obtain reproducible behavior characteristic of interhalogen compounds.[12–14]

On the whole, the results of the present study confirm these observations. Figure 1 indicates that in the absence of macro amounts of another halogen a substantial part of the astatine is present in something other than the elemental form, and comparison with Figure 2 shows that small amounts of iodine behave in a remarkably similar fashion. The $HI^+$ and $HAt^+$ appearing in these figures may result either from hydrolysis with traces of water or from substitution reactions with organic hydrogen.

Our failure to observe $At_2$ does not allow us to draw any definite conclusions about the equilibrium $2At \rightleftharpoons At_2$. When the astatine was distilled directly from the platinum into the spectrometer a platinum astatide may have been decomposing, and the At atoms formed may not have had time to combine to $At_2$ molecules. In the other experiments, most or all of the $At^+$ observed may have arisen from fragmentation of vapor-phase compounds.

As we might have expected, addition of excess iodine, bromine, or chlorine converts a large part of the astatine into the corresponding monohalide. Although higher astatine bromides and chlorides might be expected to exist, they would probably not form under the rather mild halogenating conditions that we have employed.

The low volatility observed for the astatine compounds probably means that we are dealing with surface adsorption effects bearing little relation to bulk vapor pressure. However, the nearly complete loss of volatility in the presence of $ClF_3$ is puzzling since under such conditions we might have expected the formation of a relatively volatile astatine fluoride.

**Acknowledgments.**—We wish to thank Mr. Milan Oselka and the Argonne cyclotron crew for its invaluable cooperation and the Chemistry Division Radiation Safety Group under Mr. Gerald Combs for its aid. We are grateful to Mr. Leon P. Moore for technical assistance.

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CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
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# Mössbauer Spectra of $SnH_4$ and Related Compounds

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The Mössbauer spectra of $SnH_4$ and a number of related organotin hydrides, organotin halides, and other compounds have been determined at 77°K. The isomer shifts (with respect to $SnO_2$) noted for the hydrides fall into two groups: $1.24 \pm 0.03$ mm/sec for compounds with at least one $CH_3$–Sn bond, and $1.42 \pm 0.04$ mm/sec for molecules not having a $CH_3$–Sn bond. The $R_nSnH_{4-n}$ spectra show the absence of a quadrupole interaction between the $Sn^{119m}$ nuclei and the electric field gradient tensor, consistent with an effect first noted by Greenwood. The relationship between this observation and the bonding in organotin compounds is examined in detail. The decomposition of $SnH_4$ at 0° to give white ($\beta$) tin has been confirmed. The infrared spectrum of *n*-butyltin trihydride is presented.

## Introduction

In a recent study[2] of the Mössbauer spectra of a number of organotin compounds, three observations relating to the systematic substitution of ligands bonded to the metal atom were noted: (1) Substitution of $sp^2$ hybridized (aromatic) C atoms for $sp^3$ hybridized (aliphatic) C atoms has only a very small effect on the isomer-shift parameter. (2) In binuclear compounds with tin–tin linkages of the type $R_3Sn–SnR_3$, no quadrupole splitting could be resolved from the resonance

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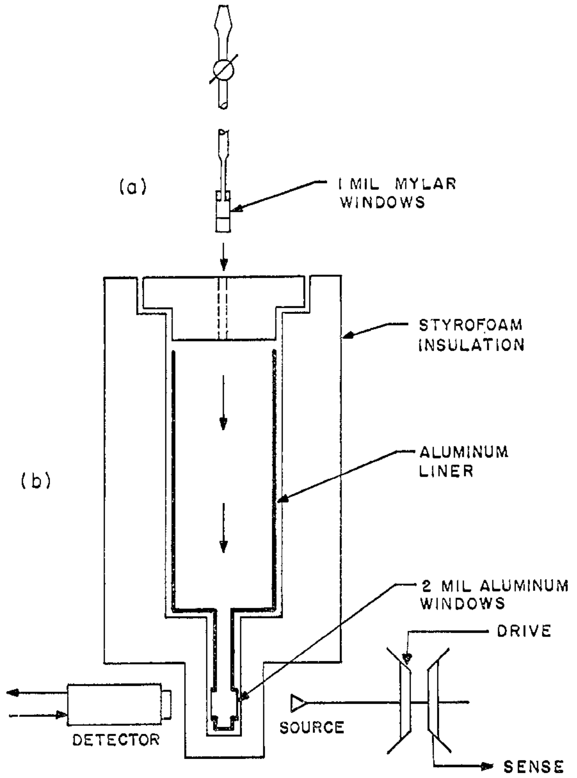

Figure 1.—(a) sample cell; (b) low-temperature cryostat.

spectrum. (3) Similarly, no quadrupole splitting could be resolved in the resonance spectrum of $(p\text{-FC}_6H_4)_3$-SnH, the only hydride which was included in the series. To elucidate the origin of these observations further, a systematic study of the Mössbauer spectra of $SnH_4$ and several related stannanes has been undertaken. Infrared and nmr data on these compounds have also been obtained and compared to published values where these exist.

## Experimental Section

The details of the parabolic motion spectrometer, which utilizes a multichannel analyzer in the time (multiscaler) mode, have been described fully elsewhere.[3] In early experiments, both $SnO_2$ and $Mg_2Sn$ were employed as host matrices for the $Sn^{119m}$ activity. Although the former gives rise to large resonance effects due to a large recoil-free fraction of emission events, the resultant resonance lines are wide ($\sim$1.5 ± 0.2 mm $sec^{-1}$) even for thin absorbers. It has recently been shown[4] that this line broadening is due to a small quadrupole interaction between the $J = {}^3/_2$ excited state of the $Sn^{119}$ nucleus and the electric field gradient due to the nearest-neighbor oxygen atoms. This line broadening is thus intrinsic to the $SnO_2$ matrix and cannot be diminished by chemical treatment of the source. On the other hand, $Mg_2Sn$ does give essentially the natural line width[5] with thin absorbers, but shows small resonance effects due to the small recoil-free fraction of emission events in this matrix. A compromise between these factors can be achieved by utilizing a source made by diffusing a small amount of $Sn^{119m}$-labeled metallic tin into palladium to make a dilute (approximately 3%) solution. This source has been described in detail elsewhere.[6] The isomer shift between our $SnO_2$ and Pd(Sn) sources is 1.46 ± 0.05 mm $sec^{-1}$ at room temperature, with the metallic source giving resonance absorptions at more negative Doppler velocities.

Stannane, $SnH_4$, was prepared by the sodium borohydride reduction of $SnCl_2$.[7] The metathesis was carried out on a standard vacuum line, and the resultant volatile products were fractionated by distilling from a trap at $-78°$ to a receiver at $-196°$. The purified stannane was transferred again by distillation into a sample cell (Figure 1) fitted with 1-mil Mylar windows and a high-vacuum stopcock. After transfer was completed, the stopcock of this cell was closed and the cell was warmed to room temperature. By directing a stream of liquid nitrogen at the windows, the stannane was condensed on the inside surface of the Mylar film. The whole cell was immediately immersed into liquid nitrogen in a Styrofoam dewar in the appropriate geometry for the Mössbauer spectrum determination.

Following accumulation of the Mössbauer data, the sample cell containing the stannane was immersed in an ice bath in such a manner that one Mylar window could be illuminated with visible radiation from an incandescent lamp without warming up the remainder of the cell. After a period of about 10 hr the illuminated window was found to be thoroughly covered on the inside with a thin layer of metallic tin from the well-known[8] thermal decomposition of $SnH_4$. The cell was reimmersed in the liquid nitrogen dewar and the Mössbauer spectrum of the metal film was determined as before. This procedure served to confirm the formation of white ($\beta$) metallic tin in the stannane decomposition, as well as to provide a calibration point on the velocity scale of the Mössbauer spectrum. The observed $SnO_2$–$\beta$-Sn isomer shift of 2.68 ± 0.03 mm $sec^{-1}$ is in good agreement with values reported earlier.[9]

Methyltin trihydride was prepared by reducing methyl stannonic acid with sodium borohydride according to the method of Pfeiffer and Lehnhardt.[10] The remaining organotin hydrides (except $i\text{-}C_3H_7SnH_3$) were synthesized from the corresponding chlorides by the method of Finholt, *et al.*,[11] using either di-*n*-butyl ether, dioxane, or diethyl ether as solvents. The sample of isopropyltin trihydride was generously made available to us by Professor H. D. Kaesz and used after vacuum line fractionation without further chemical treatment. Di-*n*-butylchlorotin hydride was made according to the method of Sawyer and Kuivila[12] by allowing equimolar quantities of $(n\text{-}C_4H_9)_2SnH_2$ and $(n\text{-}C_4H_9)_2SnCl_2$ to react. The alkyl- and aryltin chlorides used as starting materials and the sample of tetramethyltin were obtained from commercial sources.[13]

Infrared spectra were obtained at room temperature on gaseous or neat liquid samples using NaCl optics with a Perkin-Elmer Model 521 grating spectrophotometer. Impurity levels judged from the infrared data are less than 1%.

Nmr data were obtained on 15% solutions of the samples in tetramethylsilane (with the solvent being used as an internal standard) on a Varian A60 spectrometer.

Mössbauer spectrum runs were programmed so that at least $10^5$ counts per channel were accumulated giving a statistical standard deviation of ±0.3%. Since the magnitude of the resonance effect, $\epsilon = (N_\infty - N_0)/N_\infty$, for these compounds is $\gtrsim$3%, the signal-to-noise ratio for the resonance peak is $\gtrsim$10:1. A typical Mössbauer spectrum is shown in Figure 2.

## Results and Discussion

**(A) Infrared and Nmr Results.**—The main purpose in obtaining infrared and nmr data on the organotin

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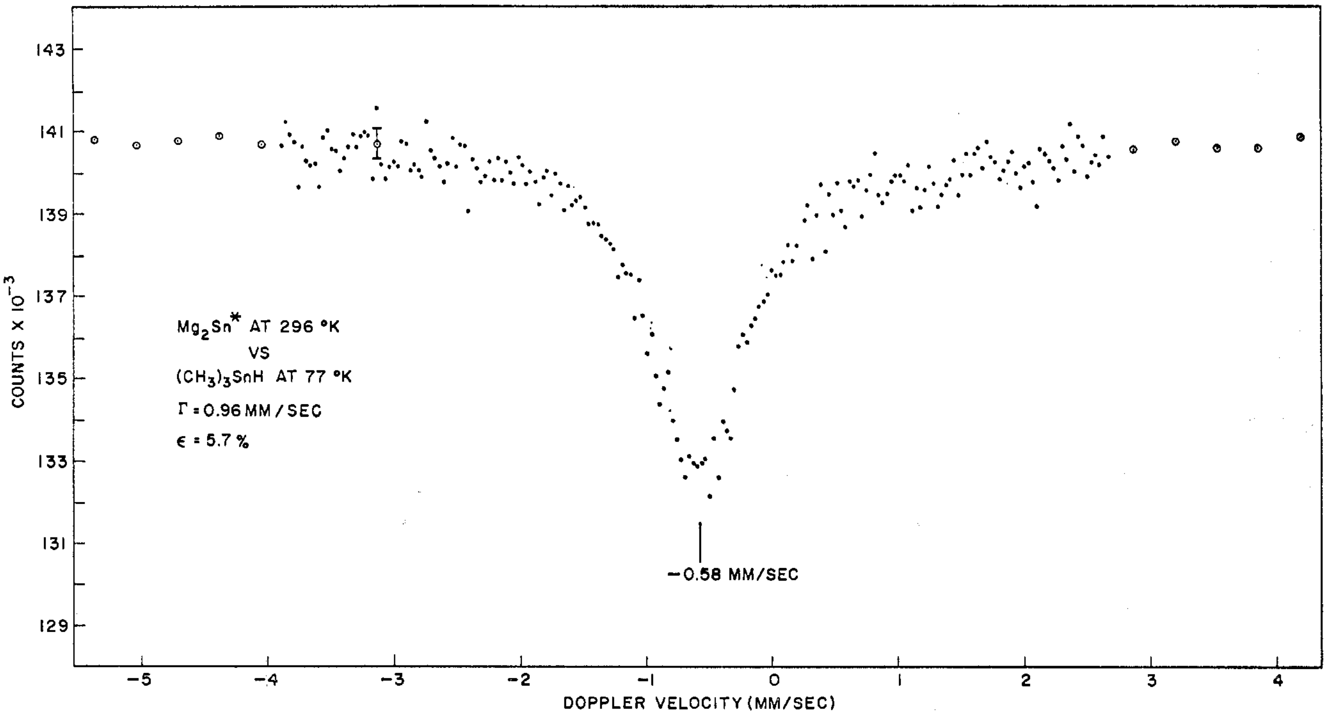

Figure 2.—Mössbauer spectrum of $(CH_3)_3SnH$ at 77°K (source $Mg_2Sn$ at 296°K).

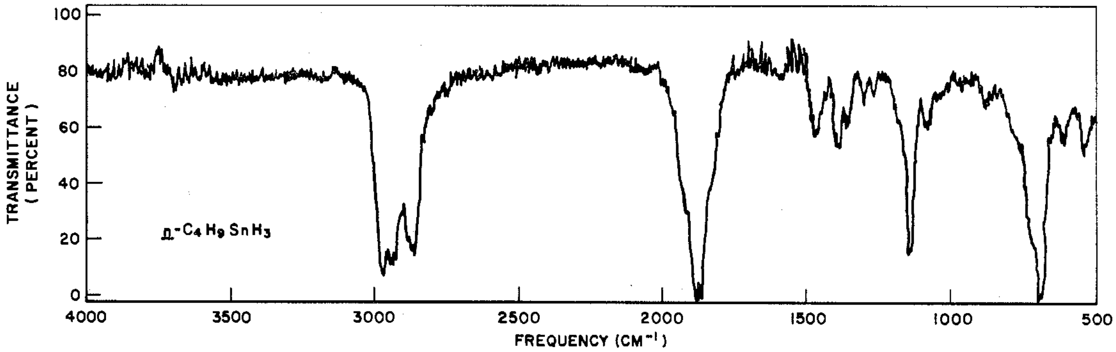

Figure 3.—Infrared spectrum of $n$-$C_4H_9SnH_3$ at 23° using NaCl optics.

hydrides was to provide a check on the chemical identity and purity of the products of the synthetic procedures employed.

The infrared spectra of $SnH_4$[14] (I), $CH_3SnH_3$[15] (II), $(CH_3)_2SnH_2$[15] (III), and $(CH_3)_3SnH$[15,16] (IV) agree with literature values, and data on the present compounds confirm their identity and purity. The infrared spectrum of $n$-$C_4H_9SnH_3$ (V) in the gaseous state is shown in Figure 3. Its spectrum shows an Sn–H absorption at 1880 $cm^{-1}$, in good agreement with the value of 1876 $cm^{-1}$ observed by Dillard and May[15] in the spectrum of II. The tin–hydrogen absorptions in $(n$-$C_4H_9)_2SnH_2$[17] (VI) and $(n$-$C_4H_9)_3SnH$[16] (VII) are in good agreement with published values, and the infrared data for the family of phenyltin hydrides similarly are consistent with values reported in the literature.[16,18]

The nmr datum on $(CH_3)_2SnH_2$ (III) which shows a $\tau$ value of 5.59 is in only modest agreement with the value of 5.24 reported by Flitcroft and Kaesz,[10] but agrees excellently with the value of 5.61 found by Clark, *et al.*[19] Other $\tau$ values observed in the present study are in good agreement with published values.[10,20,21] The only wide discrepancy exists between the chemical shift of 5.21 observed for $(n$-$C_4H_9)_3SnH$ and the value 7.93 reported by Potter, *et al.*[20] It is felt that, despite the lack of any quantitative correlation of chemical shift with number of organic groups, the trends exhibited would place the tin–proton resonance for this monohydride in the more downfield position. The chemical shifts for $(n$-$C_4H_9)_2SnH_2$ and $(n$-$C_4H_9)_2SnHCl$, 5.36 and 2.72, respectively, show the expected behavior of a lower $\tau$ value for the latter compound due to the replacement of one of the hydrogens of the dihydride by a (more electronegative) chlorine atom.

**(B) Quadrupole Splitting.**—The Mössbauer pa-

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rameters obtained in the present investigation are summarized in Table I. The absence of resolvable quadrupole splitting for all the hydrides for which such splitting might have been expected [*i.e.*, for all absorbers except $SnH_4$] is immediately apparent. This observation supports the data on $(p\text{-}FC_6H_4)_3SnH$ reported earlier,[2] as well as the results on a number of alkyl- and aryltin monohydrides and di-*n*-propyltin dihydride reported by Aleksandrov, *et al.*[22] Since the latter data were obtained solely by the use of an $Sn^{119m}O_2$ source giving line widths of 1.15–1.20 mm $sec^{-1}$, the possible presence of small quadrupole splittings was not definitely excluded. The present data show unambiguously that the resonance line widths for the organotin hydrides are no wider for comparable absorber thicknesses than are the widths observed in the resonance spectra of $(CH_4)_4Sn$ and $(C_6H_5)_4Sn$.

TABLE I

MÖSSBAUER PARAMETERS FOR $SnH_4$ AND RELATED COMPOUNDS

| | Absorber (77°K) | Source (296°K) | Isomer shift,[a] mm $sec^{-1}$ | Quadrupole splitting, mm $sec^{-1}$ | Line width,[b] mm $sec^{-1}$ |
|---|---|---|---|---|---|
| I | $SnH_4$ | $SnO_2$ | 1.27 | 0 | 1.48 |
| II | $CH_3SnH_3$ | $Mg_2Sn$ | 1.24 | 0 | 1.04 |
| III | $(CH_3)_2SnH_2$ | $SnO_2$ | 1.23 | 0 | 1.54 |
| | | $Mg_2Sn$ | 1.22 | 0 | 1.27 |
| IV | $(CH_3)_3SnH$ | $Mg_2Sn$ | 1.24 | 0 | 0.96 |
| V | $n\text{-}C_4H_9SnH_3$ | Pd(Sn) | 1.44 | 0 | 0.94 |
| VI | $(n\text{-}C_4H_9)_2SnH_2$ | Pd(Sn) | 1.42 | 0 | 1.33 |
| VII | $(n\text{-}C_4H_9)_3SnH$ | Pd(Sn) | 1.41 | 0 | 1.03 |
| VIII | $C_6H_5SnH_3$ | Pd(Sn) | 1.40 | 0 | 1.03 |
| IX | $(C_6H_5)_2SnH_2$ | Pd(Sn) | 1.38 | 0 | 1.01 |
| X | $(C_6H_5)_3SnH$ | Pd(Sn) | 1.39 | 0 | 1.10 |
| XI | $i\text{-}C_3H_7SnH_3$ | $SnO_2$ | 1.40 | 0 | 1.50 |
| | | $Mg_2Sn$ | 1.46 | 0 | 0.99 |
| XII | $(CH_3)_4Sn$ | $Mg_2Sn$ | 1.22 | 0 | 1.21 |
| XIII | $(n\text{-}C_4H_9)_2SnHCl$ | Pd(Sn) | 1.56 | 3.34 | 1.06 |
| XIV | $(n\text{-}C_4H_9)_3SnCl$ | Pd(Sn) | 1.58 | 3.40 | 0.92 |
| XV | β-Sn | $SnO_2$ | 2.68 | 0 | 1.51 |
| XVI | $SnO_2$[d] | $SnO_2$ | 0 | 0 | 1.45 |
| | | $Mg_2Sn$ | −1.82[c] | 0 | 1.32 |
| | | Pd(Sn) | 1.46[c] | 0 | 1.29 |
| XVII | $Mg_2Sn$[d] | $SnO_2$ | 1.82 | 0 | 1.38 |
| | | $Mg_2Sn$ | 0[c] | 0 | 0.93 |

[a] With respect to the $SnO_2$ source. All values ±0.06 mm $sec^{-1}$. [b] Full width at half-maximum of the resonance line. All values ±0.04 mm $sec^{-1}$. [c] Isomer shift from $SnO_2$. [d] Absorber at 296°K.

These results are in agreement with an observation made by Greenwood[23] pertaining to the magnitude of the quadrupole splitting in the Mössbauer spectra of organotin compounds: *such quadrupole splitting will be observed only if one or more of the atoms directly bonded to the tin atom in an asymmetric compound has one or more unshared electron pairs.* That the magnitude of the quadrupole interaction depends on the presence of such nonbonding electrons can be understood in terms of $p\pi$–$p\pi$ electron donation by the ligands into the available AO's of the metal atom. This transfer of charge results in a distortion of the spherically symmetric $sp^3$ hybrid bonds used by the tin atom in the primary metal atom-to-ligand interaction. The large electrical field gradients which arise from this distortion are observed as easily resolved quadrupole splittings in the Mössbauer spectra. In $(CH_3)_3SnCl$ the observed splitting is[24] 3.09 ± 0.07 mm $sec^{-1}$, and in $(C_6H_5)_3SnCl$ the reported quadrupole splitting is[25] about 2.5 mm $sec^{-1}$. In both molecules the distortion of the tetrahedrally symmetric charge distribution arises from electron donation to the metal atom by the unshared pairs on the halogen ligand.

This origin of the quadrupole splitting is further illustrated by the fact that $(n\text{-}C_4H_9)_2SnHCl$ shows a quadrupole splitting of 3.34 ± 0.03 mm $sec^{-1}$, as shown in Table I. The electric field gradient giving rise to this splitting arises from the presence of the halogen ligand in the molecule.

The present data further serve to eliminate an alternative explanation for the absence of quadrupole splitting in the resonance spectra. This alternative explanation involves the electronegativity difference in the tin–ligand bonds and the resulting charge asymmetry caused by this difference. Using the group electronegativity calculations of Hinze, Whitehead, and Jaffé,[26] the electronegativity difference, $\Delta X$, in the $CH_3$–Sn bond is calculated to be 0.61 unit, the $\Delta X$ value in the Sn–H bond is 0.38 unit, and the $\Delta X$ value in the Sn–I bond is 0.49 unit. The quadrupole splitting observed in the Mössbauer spectra of related tris(alkyl)- and tris(aryl)tin iodides has also been reported.[2] The values for $(p\text{-}FC_6H_4)_3SnI$ and $[(CH_3)_2C(C_6H_5)CH_2]_3SnI$ are 1.92 and 2.40 mm $sec^{-1}$, respectively, at 77°K. Since the difference in the $CH_3$–Sn and Sn–I bond electronegativity difference, $\delta(\Delta X)$, is 0.12 unit while the $\delta(\Delta X)$ value for the $CH_3$–Sn and Sn–H bond pair is 0.23 unit, it is clear that electronegativity differences alone do not account for the absence of resolvable quadrupole splitting in the spectra of the hydrides listed in Table I. Moreover, since quadrupole-splitting energies as small as $2 \times 10^{-8}$ ev (0.25 mm $sec^{-1}$) could have been resolved from the present data, it is seen that if electronegativity differences alone contribute to the magnitude of the quadrupole interaction, the effect of much smaller $\delta(\Delta X)$ could have been observed.

The most striking evidence with respect to the $\delta(\Delta X)$ reasoning is the observation by Aleksandrov, *et al.*,[22] that the Mössbauer resonance spectrum of triphenyltin lithium, $[(C_6H_5)_3SnLi]$, also shows only a single resonance line. Any asymmetry in the electron density

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introduced by the Sn–Li bond must be distributed to the other three bonding orbitals in such a way that an essentially symmetric charge distribution results.

Additional data on binuclear tin compounds further strengthen the reasoning which implicates nonshared electron pairs on the ligands in determining the magnitude of the electric field gradient. As was pointed out earlier,[27] none of the binuclear tin compounds such as $[(C_2H_5)_3Sn]_2$,[28] $[(C_6H_5)_3Sn]_2$,[27] and various ring-substituted compounds shows resolvable quadrupole splitting in the resonance spectra. On the other hand, binuclear compounds such as $[(C_2H_5)_2SnCl]_2$[25] containing at least one ligand having an unshared electron pair give rise to very large quadrupole interactions, the energy in the latter case amounting to $2.4 \times 10^{-7}$ ev ($\sim$3 mm $sec^{-1}$). In the hexaalkyl and hexaaryl binuclear compounds, the value of $\delta(\Delta X)$ is 0.61. Since this is larger than the $\delta(\Delta X)$ value for the $CH_3$–Sn and Sn–Cl bond pair, it is seen that the presence of an unshared electron pair on one of the tin atom ligands is a necessary condition for observing the quadrupole moment–electric field gradient interaction in the resulting Mössbauer spectra. In addition, the data on the binuclear compounds lead to the conclusion that the overlap between the 6p orbitals on the tin atom and the $\pi$-electron system of the conjugated ring is too small to distort the charge symmetry around the tin nucleus. Moreover, any appreciable electron donation from the ring system to the tin atom would have a concomitant effect on the isomer shift of the resonance spectrum. That such effects are absent has been pointed out previously.[2]

The Hamiltonian which describes the quadrupole interaction between a nucleus with a nuclear quadrupole moment, $Q$, and the electric field gradient tensor, $\nabla E$, is

$$\mathcal{H} = Q \cdot \nabla E \tag{1}$$

For a nucleus with a spin state $I = {}^3/_2$, it can be shown[3] that the eigenvalues for (1) are

$$E_Q = \frac{eqQ}{4I(2I-1)}\,[3m_I^2 - I(I+1)]\left(1 + \frac{\eta^2}{3}\right)^{1/2} \tag{2}$$

in which $q$ is the negative of the electrostatic field gradient due to charges on ligands, $m_I$ is the magnetic quantum number, and $\eta$ is an asymmetry parameter related to the three components of the electric field gradient. In the case of $Sn^{119}$, the two allowed values for $m_I$ are $|{}^1/_2|$ and $|{}^3/_2|$ for the first excited state. When the tin atom occupies a lattice site where the electric field gradient tensor is nonvanishing (*i.e.*, $q \neq 0$), the ${}^3/_2{}^+$ state is split into two levels, one of which is raised in energy by an amount

$$E_Q\left(m_I = \frac{3}{2}\right) = \frac{eqQ}{4}\left(1 + \frac{\eta^2}{3}\right)^{1/2} \tag{3}$$

and the other level is lowered by an identical amount.

The electric field gradient at the tin nucleus is attenuated by the electrons (both bonding and nonbonding) which occupy a region of space between the nucleus and the position of the charges of the ligands. This attenuation is usually expressed in terms of a shielding factor, $\gamma_\infty$, such that the ligand charge effective in determining the electric field gradient at the nucleus is $q(1 - \gamma_\infty)$, so that

$$E_Q = \frac{eqQ}{2}\,(1 - \gamma_\infty)\left(1 + \frac{\eta^2}{3}\right)^{1/2} \tag{4}$$

In organotin compounds in which none of the ligand atoms directly bonded to the metal atom has unshared electron pairs, the primary valence electron orbital hybridization involves 5s and 5p metal orbitals. This hybridization gives rise to four $sp^3$ orbitals oriented in the usual tetrahedral configuration. If one of the ligands has an appreciably different electronegativity than the remaining three, it must be concluded from the present data that all four bonds reflect this disparity, without altering the basic $sp^3$ hybridization. In going from $(C_6H_5)_4Sn$ to $(C_6H_5)_3SnLi$, the electron density in all four bonds reflects the decrease in the total ligand electronegativity, without, however, changing the symmetry of the electron density around the metal atom.

In organotin compounds in which one or more of the nearest neighbor atoms has an unshared electron pair, the orbital containing this pair can overlap with one of the three 6p orbitals of the tin atom in a $p\pi$–$p\pi$ interaction. Such an interaction will give rise to an appreciable distortion of the charge symmetry around the metal atom, and the interaction between the nuclear quadrupole moment of the $Sn^{119}$ atom with the electric field gradient generated by the nontetrahedral charge distribution is observed in the corresponding Mössbauer spectra.

Finally, it is interesting to relate these data to the interpretation given by Boyle, *et al.*,[29] of the Mössbauer data for tetragonal SnO, which shows a quadrupole splitting of 1.6 mm $sec^{-1}$. The field gradient which gives rise to this splitting is ascribed as due to the unshared electron pair which occupies one vertex of the square-based pyramidal structure of SnO( $D_{4h}{}^7$-P4/nmm).[30] The major difference between the origin of the field gradient in SnO as compared to the organotin compounds investigated in the present study is the fact that in the oxide the unshared pair is presumably localized mainly near the metal atom and contributes to the field gradient which is implicit in the pyramidal structure. In the latter group of compounds, the "active" unshared pair is localized primarily in a $\pi$ interaction between the metal atom and the ligand. In the

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(27) For a summary of Mössbauer data on iron and tin organic compounds, see R. H. Herber, Advisory Panel on the Mössbauer Effect, International Atomic Energy Agency, Vienna, May 1965, in press.

(28) V. I. Goldanskii, V. Ya. Rochev, and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, **156**, 909 (1964).

(29) A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, *Proc. Phys. Soc.* (London), **79**, 416 (1962).

(30) W. J. Moore and L. Pauling, *J. Am. Chem. Soc.*, **63**, 1392 (1941).

absence of this interaction (*e.g.*, for ligands not possessing such unshared pairs), the electric field gradient vanishes at the Mössbauer atom lattice point.

**(C) Isomer Shift.**—The isomer shifts with respect to $SnO_2$ which are observed in this study are also summarized in Table I and are seen to be similar to those reported[27] for other organotin compounds. Closer examination shows that the isomer shifts for the hydrides fall into two distinct groups. One group shows a shift of 1.24 ± 0.03 mm $sec^{-1}$, while the other group shows a shift of 1.42 ± 0.04 mm $sec^{-1}$. This grouping effect is clearly outside of experimental error and is also evident from the data of Aleksandrov, *et al.*[22] The presently available data show that organotin compounds of the type $R_nSnH_{4-n}$ (R is either an alkyl or aryl group) in which there is at least one $CH_3$–Sn bond will have isomer shifts which are ~0.18 mm $sec^{-1}$ more negative than the shifts for organotin compounds with no methyl–tin bonds. This distinctive behavior of methyl–tin compounds is clearly not due primarily to steric factors, since such factors would be noted in the Mössbauer parameters for the systematic replacement series $i$-$C_3H_7$, $n$-$C_4H_9$, $i$-$C_4H_9$, $C_6H_5$. That such steric effects are absent is clearly seen from the data in Table I and ref 22.

Finally, it is evident from these data that the observed isomer shift for $SnH_4$ is considerably smaller than that which would have been predicted from simple electronegativity considerations. The correlations suggested earlier[2,31] for isomer shifts of $SnA_4$ molecules give a value for $SnH_4$ which is approximately 0 4 mm $sec^{-1}$ larger than the value observed experimentally. A detailed examination of the relationship between ligand electronegativity, bond character, and steric parameters of organotin compounds and their corresponding Mössbauer parameters is currently under way in these laboratories.

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[31] V. I. Goldanskii, "The Mössbauer Effect and Its Applications in Chemistry," Consultants Bureau, New York, N. Y., 1964.

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# Magnetic Susceptibility and Mössbauer Results of Some High-Spin Iron(II) Compounds[1a]

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Using iron(II)–pyridine complexes as examples, we have explored the relation between the average magnetic moments, $\mu$, and the Mössbauer parameter, $\Delta E_Q$, assuming that the iron nucleus is in an environment of tetragonal symmetry—a distortion from octahedral symmetry. $\Delta E_Q$ is very sensitive to small deviations from octahedral symmetry whereas the average magnetic moment is insensitive.

## Introduction

The applications of the Mössbauer effect to the study of chemical compounds has led to an investigation of the physical meaning of the parameters $\Delta E_Q$ (quadrupole splitting) and the isomer shift. A general theoretical treatment of the problem[2] has revealed that $\Delta E_Q$ and magnetic moment, $\mu$, are directly related, and both can be used for investigating the asymmetry of the environment of the iron nucleus.

The treatment for low-spin iron(III) compounds is discussed elsewhere.[2] Here we are concerned solely with high-spin iron(II) compounds, and we have used results obtained for a series of pyridine derivatives as illustrated examples.

## Experimental Section

The methods by which the pyridine compounds were prepared were as follows.

(i) **Fe(py)$_4$Cl$_2$.**—Pure iron powder (5 g) was gradually added to 15 ml of AnalaR concentrated hydrochloric acid. When the hydrogen had ceased to evolve, about 20 ml of methanol was added and the solution was filtered into a flask containing 100 ml of pyridine under a nitrogen atmosphere. Intense yellow crystals separated out immediately. The mixture in the flask was allowed to stand overnight in the inert gas atmosphere. The crystals were filtered off and recrystallized from pyridine and were filtered and dried in a vacuum desiccator. *Anal.* Calcd for Fe(py)$_4$Cl$_2$: Fe, 12.6; C, 54.2. Found: Fe, 12.6; C, 53.4.

(ii) **Fe(py)$_4$Br$_2$.**—This was prepared according to the method of Weinland, *et al.*[3] Bromine (1.5 ml) was slowly added to 3 g of pure iron powder in 20 ml of methanol. When the reaction had ended, the solution was filtered with stirring into a flask containing 50 ml of pyridine. The mixture was allowed to

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[2] R. M. Golding, to be published.

[3] R. Weinland, K. Effinger, and V. Beck, *Arch. Pharm.*, **265**, 352 (1927).