BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3034—3036 (1970)

The Mössbauer Effect in Triethyltin Phenyl Derivatives

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(Received February 19, 1970)

Substituent effect of triethyltin phenyl derivatives was investigated by means of the ^{119}Sn Mössbauer effect. The isomer shifts obtained for these compounds fall into the range -0.15—-0.18 mm/sec with respect to Pd$^{119\text{m}}$Sn source. *p*-Cl and *m*-Cl derivatives show broadened spectra, which may be ascribed to an unresolved quadrupole splitting. This small quadrupole interaction may be interpreted in terms of the partial ionicity of the bond formed between tin and carbon in phenyl group.

The Mössbauer effect in organotin compounds provides useful information on the nature of the chemical bond formed by tin atom. The tin atom, which belongs to group IV, may act effectively as a probe embedded in organic compounds. Quadrupole splitting takes place by low symmetric distribution of the valence electron. Thus, it provides a measure of the partially ionic character of sp^3 hybrid bonding. Tin organic compounds have similar values of the isomer shift. A study of the isomer shift for a series of compounds may supply a great deal of information.

In the present paper, the Mössbauer spectra of triethyltin phenyl derivatives (X-$C_6H_4SnEt_3$, X= H, *p*-CH_3, *m*-CH_3O, *p*-Cl, *m*-Cl) at 80°K and the effects of substituent are described. The compounds showed essentially the same isomer shift. The Mössbauer spectra for *p*-Cl and *m*-Cl derivatives gave single but broadened lines. The broadened line may be decomposed into an unresolved quadrupole doublet, and it seems reasonable to expect that the chlorine atom makes the Sn-C bond character partially ionic through phenyl group due to its inductive effect.

Experimental

The Doppler velocity spectrometer has an electromechanical negative feedback system.[1-4] The circuit for this system is shown in Fig. 1. The velocity signal is 12.5 Hz sawtooth or triangular wave, *viz*, the constant acceleration mode. The velocity scale has been cali-

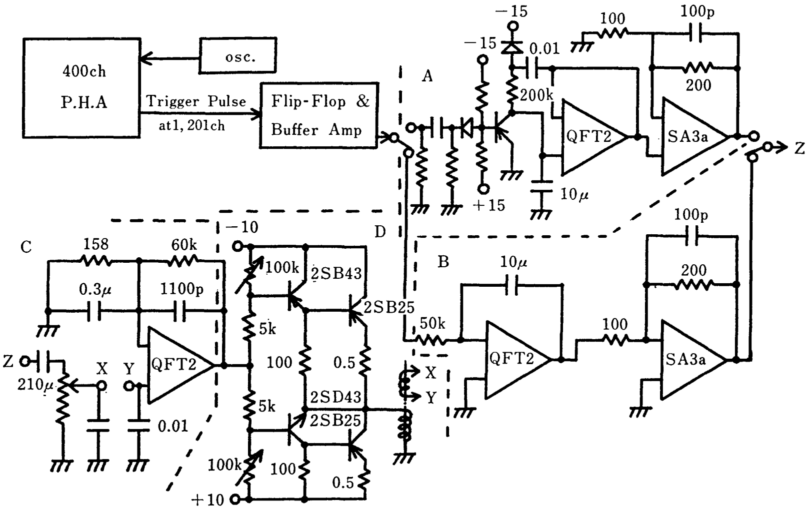

Fig. 1. Electromechanical feedback system for Mössbauer effect experiment. A; sawtooth wave B; triangular wave C; control circuit D; power circuit

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brated by the isomer shift values of β-Sn and SnO_2. For the triangular wave mode, zero velocity corresponds to the middle of the 100 and 101 channels and also that of the 300 and 301 channels. The isomer shift can be obtained with a good reproducibility within one channel. The source was $Pd^{119m}Sn$ containing about 0.2 mCi ^{119m}Sn. The source was used at room temperature, while the absorber were solidified by cooling with liquid nitrogen in the cryostat shown in Fig. 2. The absorbers are liquid at room temperature and were injected into the cell by a syringe. The cell is made of brass. The windows of the cell are of myler of 25 μ thickness. All of the Mössbauer spectra were obtained with absorber thickness 50—60 mg/cm² Sn.

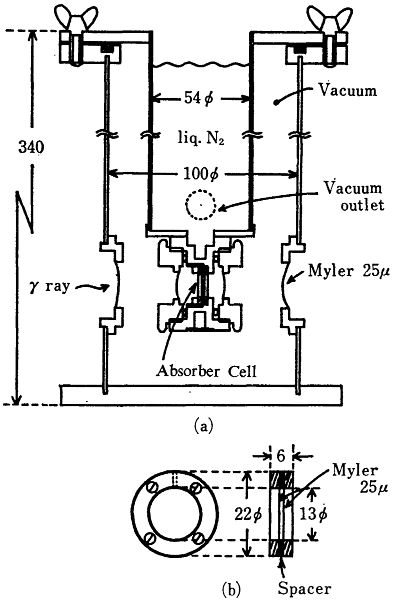

Fig. 2. Cryostat (a) and absorber cell (b). unit; mm

Triethyltin phenyl derivatives were prepared from triethyltin bromide and appropriate phenylmagnesium bromides in dry ether by the Grignard reaction.⁵⁾ They were purified by repeated fractional distillation at reduced pressure until GLC showed only one peak. They were identified by means of elementary analysis and infra- and farinfra-red spectra. The compounds can be synthesized easily, but the phenyl derivatives with polar functional group have not been synthesized as yet, for example, Grignard reagent cannot be made in dry ether or dry tetrahydrofuran in the case of m-NO_2 C_6H_4Br.

Results and Discussion

The isomer shifts in organotin compounds such as tetravalent tin fall in a narrow range. Tetravalent tin forms $5sp^3$ hybridization in many cases. An increase in s-electron density at the tin nucleus corresponds to an increase in isomer shift. Difference in s-electron density at the tin nucleus in various compounds mainly depends on the contribution from 5s-electron density. However, it is important to consider not only 5s-electron density but also the shielding of the 5s-electron by the 5p-electron. It may be considered that the partial ionicity of a bond in a sp^3 hybridization leads not only to a decrease in s-character but also to the compensation of a decrease of s-electron density through the decrease of shielding by the 5p-electron. For tin compounds, the electric field gradient at the tin nucleus may appear as a result of the asymmetric distribution of the valence electron. Partial ionicity of a bond in sp^3 hybridization leads to an unbalanced state in a p-character of four bonding orbitals. Thus, it is important to obtain a correlation between the isomer shift and quadrupole splitting. A more theoretical treatment is required for this.

It has been suggested that only nonuniformity in dative π-bonding abilities of the atoms bonding to the tin atom can produce an electric field gradient large enough to give an observable quadrupole splitting.⁶⁾⁷⁾ However, in the Mössbauer spectra of compounds of the type $(C_6F_5)_{4-n}SnX_n$ ($X=C_6H_5$, CH_3, p-$CH_3C_6H_4$, $n=1,2,3$), observation of quadrupole splitting has been reported and interpreted in terms of electrostatic inductive and more predominant mesomeric effect of the pentafluoro phenyl group.⁸⁾ Similar results for R_3SnX ($R=CH_3$, C_6H_5, $X=CF_3$, C_6F_5, C_6Cl_5, $C{\equiv}CC_6H_5$) have shown that the quadrupole splitting can be induced by electrostatic inductive effects alone.⁹⁾ Recently, it has been reported that $(CH_3)_3Sn(p\text{-}F\text{-}C_6H_4)$ exhibits a single broader line suggesting unresolved splitting.¹⁰⁾

We observed that the inductive effect of sub-

TABLE 1. MÖSSBAUER PARAMETERS FOR TRIETHYLTIN PHENYL DERIVATIVES

Compounds$^{a)}$	I.S. (vs. $Pd^{119m}Sn$)$^{b)}$ mm/sec	Q.S. mm/sec
H-$PhSnEt_3$	−0.15	0
p-$CH_3PhSnEt_3$	−0.15	0
m-CH_3O-$PhSnEt_3$	−0.15	0
p-Cl-$PhSnEt_3$	−0.18	0.48±0.05
m-Cl-$PhSnEt_3$	−0.18	0.48±0.05

a) $Ph=C_6H_4$, $Et=C_2H_5$
b) ±0.03 mm/sec

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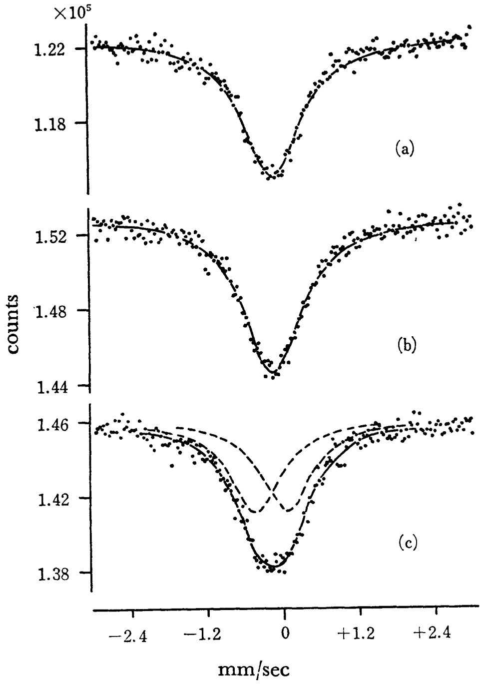

Fig. 3. Mössbauer spectra of triethyltin phenyl derivatives.
(a) $C_6H_5Sn(C_2H_5)_3$
(b) *m*-$CH_3OC_6H_4Sn(C_2H_5)_3$
(c) *p*-$ClC_6H_4Sn(C_2H_5)_3$

stituent causes a small quadrupole splitting. The results are summarized in Table 1. The isomer shift and quadrupole splitting are presented in the first and second columns of the table, respectively. A few examples of the spectra are shown in Fig. 3. The isomer shifts are shown relative to $Pd^{119m}Sn$ source, and all the numerical values are given in mm/sec. The isomer shifts of β-Sn and SnO_2 are +1.11 mm/sec and −1.58 mm/sec with respect to $Pd^{119m}Sn$ source, respectively. For X=H, *p*-CH_3, *m*-CH_3O in triethyltin phenyl derivatives X-$PhSnEt_3$, sharp, single lines with a half width of 1.14 mm/sec were observed. For *p*-Cl and *m*-Cl derivatives, however, apparently about 20 per cent broader, unsplit lines were observed. The isomer shifts were nearly equal within experimental error. The solids lines in Fig. 3(a), (b) are the single Lorentzian best fitted. However, the spectra obtained for *p*-Cl and *m*-Cl derivatives are fitted not by the single Lorentzian but by the overlap of two Lorentzians with a half width of 0.96 mm/sec (Fig. 3(c)). The broadened lines for *p*-Cl and *m*-Cl derivatives are possibly due to an unresolved quadrupole doublet. The small quadrupole splitting may be attributed to the increased ionicity of the Sn-C bond due to the inductive effect of chlorine atom. The *s*-character decreases through partially ionic character of the bond, but decreased *p*-character also compensates the decrease of the *s*-electron density at the tin nucleus through decreased shielding. Thus the increase of ionicity of the bond may not cause considerable change in isomer shift.

By means of the measurements of the electric dipole moment of the trimethyltin *p*-phenyl derivatives (*p*-$XC_6H_4Sn(CH_3)_3$, X=H, CH_3, CH_3O, $N(CH_3)_2$, Cl, Br), it has been concluded that for other derivatives with the exception of halogen derivatives, $d\pi$–$p\pi$ bonding ($(CH_3)_3Sn^{-}={}^{+}C_6H_4X$), which compensates the contribution due to the difference of electronegativity between tin and carbon ($(CH_3)_3Sn^{+}—{}^{-}C_6H_4X$), may be present, but the negative inductive effect of the halogen atom outweighs the positive mesomeri, *i. e.*, $d\pi$–$p\pi$ bonding is not indicated in the halogen substituted tin compounds.[11,12] For triethyltin phenyl derivatives, the rates of electrophilic cleavage of phenyl-tin bond are rather small for *p*-Cl and *m*-Cl derivatives in comparision with those of others.[5]

From a consideration of the inductive effect caused by the substituents, the Mössbauer spectra of the derivatives with polar functional group, *e. g.*, *m*-$NO_2PhSnEt_3$, *p*-$NO_2PhSnEt_3$, *etc.*, can be measured, but the preparation of the compounds has not been achieved as yet.

The samples were kindly supplied by Professor H. Hashimoto of Department of Synthetic Chemistry, Tohoku University.[5]

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