^{119}Sn-Mössbauer and ^{1}H- and ^{55}Mn-NMR Spectroscopic Studies of a Series of Compounds, $R_{3-x}X_xSn\text{-}Mn(CO)_5$

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The electronic configuration around the tin atom for a series of organotin-manganese compounds, $R_{3-x}X_xSn$–$Mn(CO)_5$, has been studied by ^{119}Sn-Mössbauer and ^{1}H- and ^{55}Mn-NMR spectroscopies. All the results obtained from these spectroscopic measurements show that the $Mn(CO)_5$ group is a stronger electron donor than the methyl, phenyl, or halogen group and that the tin-manganese bond prefers the sσ-character whereas the tin-halogen bond prefers the pσ-character. The relationship between the ^{55}Mn-chemical shift and the ^{119}Sn-isomer shift indicates some σ-electron withdrawal from manganese to tin. The phenyl group reduces the magnitude of quadrupole splitting more than the methyl group; this fact may be due to the mesomeric effect of the phenyl group through the π-bond between tin and ligand atoms. The relationship among the ^{119}Sn-isomer shift, the ^{1}H-chemical shift, and the coupling constant $J(^{119}Sn\text{-}^1H(CH_3))$ is also shown.

The Mössbauer spectroscopy in ^{119}Sn has been used to study a wide variety of organotin compounds as well as inorganic compounds.[1,2] The two Mössbauer parameters which are common to most studies, the isomer shift and the quadrupole splitting, have been used to elucidate the electronic configuration around the tin atoms, but there are a number of contradictions in these explanations.[3-5] Mössbauer spectroscopic studies of many compounds containing tin–transition-metal bonds, such as tin–iron tin–cobalt, and tin–manganese bonds, have been reported.[2,6-10] Mössbauer and ^{1}H-NMR spectroscopic studies have been published on alkyltin hydrides[11] and a series of compounds, $(CH_3)_{4-x}SnM_x$ (M represents metal carbonyl derivatives).[6,12] In these studies, the two "probe" atoms are used to derive information about the nature of the chemical bond pertaining to a portion of the whole molecule. We have studied a number of organotin compounds by means of Mössbauer spectroscopy,[13-16] and a number of organometallic compounds involving metal-metal bonds by means of IR and NMR spectroscopies.[17] In the present paper, three kinds of atoms, ^{119}Sn, ^{55}Mn, and ^{1}H, were used as probes to get information as to the electronic configuration, especially around the tin atom in the $R_{3-x}X_xSn$–$Mn(CO)_5$ type of compounds, where X is Cl or Br and where R is a methyl or phenyl group.

Experimental

Preparation of Compounds. All the compounds except $Cl_2(CH_3)Sn$–$Mn(CO)_5$, $Br(CH_3)_2Sn$–$Mn(CO)_5$ and $Br_2(CH_3)$-Sn–$Mn(CO)_5$ were prepared by the methods of Gorsich[18] and Graham.[19] Those three compounds were prepared as has previously been reported.[17] Carbon and hydrogen analyses were performed by Mr. Masuda for all the compounds. The purity was also checked by IR, NMR, and/or Mössbauer spectroscopies.

Mössbauer Spectra. Measurements were made as has previously been described.[20] The ^{119}Sn-Mössbauer spectra were obtained against a $Ba^{119m}SnO_3$ source drived at room temperature. The sample was used as an absorber and was kept at 79°K in a cryostat. The pertinent isomer shifts are reported with respect to the centroid of a barium stannate spectrum at room temperature. The velocity scans were calibrated with ^{57}Fe-enriched iron foil and a source of ^{57}Co diffused into copper foil, both kept at room temperature.

NMR Spectra. The ^{1}H-NMR data were obtained on dichloromethane solutions of the samples using a JNM-4H-100 spectrometer at room temperature, where the dichloromethane was used as the internal standard. The ^{1}H-chemical shift values listed in Table 1 were recalculated with respect to tetramethylsilane (TMS). The ^{55}Mn-NMR measurements were made as has been described elsewhere.[17]

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Table 1. ^{119}Sn-Mössbauer and NMR (^{55}Mn and ^{1}H) parameters for $R_{3-x}X_xSn\text{-}Mn(CO)_5$ compounds

		I.S. (mm/sec)	Q.S. (mm/sec)	^{55}Mn chemical shift (ppm)[a]	^{1}H chemical shift (ppm)[b]	$J(^{119}Sn\text{-}^{1}H(CH_3))$ (Hz)
1	$Cl_3Sn\text{-}Mn(CO)_5$	1.68	1.57	2024		
2	$Cl_2PhSn\text{-}Mn(CO)_5$	1.68	2.36	2278		
3	$Cl_2(CH_3)Sn\text{-}Mn(CO)_5$	1.68	2.62	2312	8.65	42.2
4	$ClPh_2Sn\text{-}Mn(CO)_5$	1.57	2.49	2460		
5	$Cl(CH_3)_2Sn\text{-}Mn(CO)_5$	1.54	2.66	2520	9.02	45.2
6	$Br_3Sn\text{-}Mn(CO)_5$	1.79	1.41	2044		
7	$Br_2PhSn\text{-}Mn(CO)_5$	1.80	2.63	2252		
8	$Br_2(CH_3)Sn\text{-}Mn(CO)_5$	1.69	2.51	2256	8.42	40.3
9	$BrPh_2Sn\text{-}Mn(CO)_5$	1.59	2.28	2468		
10	$Br(CH_3)_2Sn\text{-}Mn(CO)_5$	1.54	2.54	2485	8.92	45.3
11	$Ph_3Sn\text{-}Mn(CO)_5$	1.41	0	2610		
12	$(CH_3)_3Sn\text{-}Mn(CO)_5$	1.33	0.61	2660	9.50	48.9

a) ^{55}Mn chemical shift is expressed relative to $KMnO_4$.
b) ^{1}H chemical shift is expressed relative to $(CH_3)_4Si$ (TMS).

Results

A single absorption line was observed in the ^{119}Sn-Mössbauer spectrum of $Ph_3Sn\text{-}Mn(CO)_5$, whereas a well-resolved pair of quadrupole split lines was found in the spectra for all the other compounds. A typical Mössbauer spectrum is shown in Fig. 1, while the numerical values for the Mössbauer parameters at 79°K are summarized in Table 1. The isomer shifts and quadrupole splittings extracted from the data are in good agreement with those reported by Karasev *et al.*[9] for $Cl_3Sn\text{-}Mn(CO)_5$, $Br_3Sn\text{-}Mn(CO)_5$, and $Ph_3Sn\text{-}Mn(CO)_5$ compounds. The quadrupole splittings are somewhat smaller than those given recently by Wynter and Chandler[12] for $Cl_3Sn\text{-}Mn(CO)_5$, $Br_3Sn\text{-}Mn(CO)_5$, and $(CH_3)_3Sn\text{-}Mn(CO)_5$ compounds, although the isomer shift values are in moderately good agreement. The values for the chemical shift of ^{1}H- and ^{55}Mn-NMR and for the coupling constants of $J(^{119}Sn\text{-}^{1}H(CH_3))$ are also listed in Table 1. No splitting of ^{55}Mn-NMR absorption due to the coupling between ^{119}Sn and ^{55}Mn was observed. It may be worth mentioning that both the $^{1}H(CH_3)$ chemical shift and the coupling constant, $J(^{119}Sn\text{-}^{1}H(CH_3))$, decrease with a decrease in the number of methyl groups attached to the tin atom.

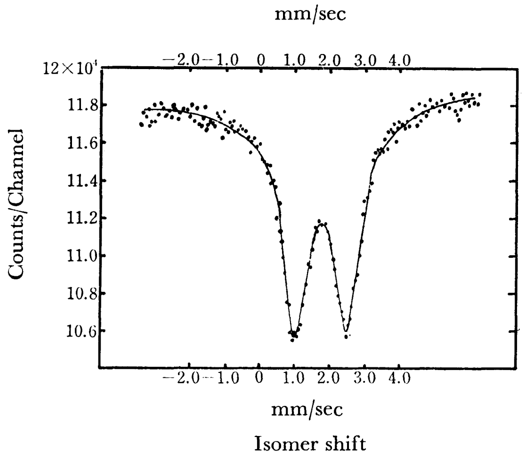

Fig. 1. A typical ^{119}Sn-Mössbauer spectrum ($Br_3Sn\text{-}Mn(CO)_5$).

Discussion

The isomer shift is proportional to the electron density at the Mössbauer nucleus, and it is dependent upon those factors which affect the electron density at the nucleus, for example, the 5s electron density on the tin atom and the extent of the shielding effect on the inner shell s-electron by the 5s, 5p, or 5d electron. It is known that the variation in the 5s electron density influences the isomer-shift value ten times more than the shielding effect in the case of tin compounds.[21] In the present case, therefore, the isomer shift values obatined are interpreted in terms of the 5s electron density.

It is clear from the data shown in Fig. 2 that the isomer shift values of $R_{3-x}X_xSn\text{-}Mn(CO)_5$ are higher than those reported previously[3] for the tin compounds, $R_{4-x}X_xSn$, at the same number of x. The isomer shift increases in the $R_{3-x}X_xSn\text{-}Mn(CO)_5$ series as the methyl or phenyl groups are successively replaced by halogen atoms. This trend is in contrast to those observed in the $R_{4-x}X_xSn$ series, where the isomer shift attains its maximum at $x=2$. These results suggest that the $Mn(CO)_5$ group is a stronger electron donor either than the methyl or phenyl group, and that the more halogen atoms are attached to tin atom, the more σ-electrons are transferred from the manganese to the tin atom.

Figure 3 illustrates the relationship between the ^{119}Sn-isomer shift and the ^{55}Mn-chemical shift; there is a smooth decrease in the chemical shift with the increase in the isomer shift. A decrease in the ^{55}Mn-chemical shift implies an increased σ-electron with-

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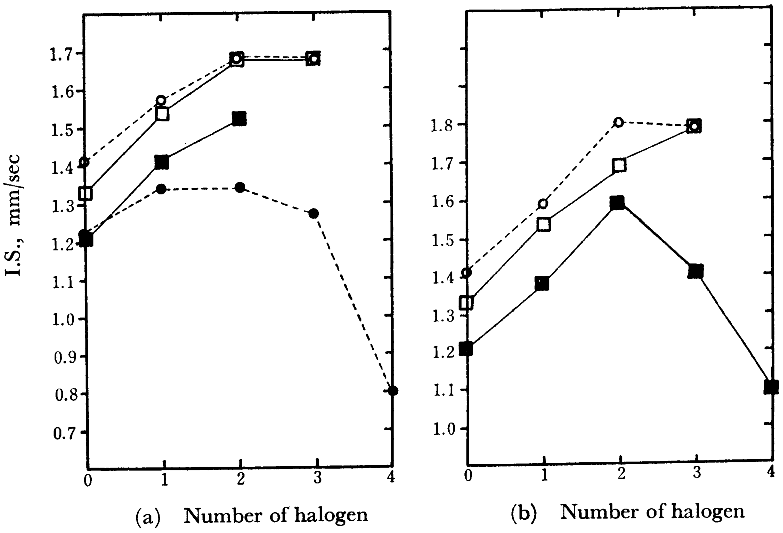
[21] J. K. Lees and P. A. Flinn, *J. Chem. Phys.*, **48**, 882 (1968).



(a) Number of halogen (b) Number of halogen

Fig. 2. Relationships between ^{119}Sn-isomer shift and number of halogen on tin atom.
(a). ■—■ represents $(CH_3)_{4-x}Cl_xSn$ compounds, ●···● $Ph_{4-x}Cl_xSn$, □—□ $(CH_3)_{3-x}Cl_xSn\text{-}Mn(CO)_5$, ○···○ $Ph_{3-x}Cl_xSn\text{-}Mn(CO)_5$ respectively.
(b). ■—■ represents $(CH_3)_{4-x}Br_xSn$ compounds, □—□ $(CH_3)_{3-x}Br_xSn\text{-}Mn(CO)_5$, ○—○ $Ph_{3-x}Br_xSn\text{-}Mn(CO)_5$ respectively.
Isomer shift data except for $R_{3-x}X_xSn\text{-}Mn(CO)_5$ are cited from the literature.[3]

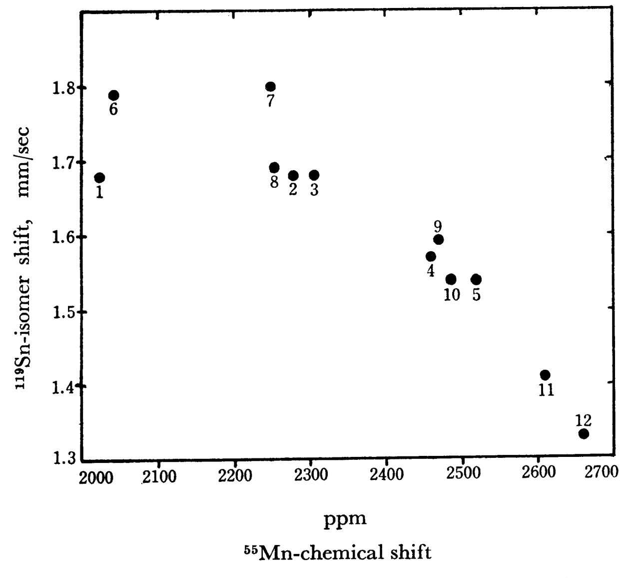


Fig. 3. The relationship between ^{119}Sn-Mössbauer isomer shift and ^{55}Mn-chemical shift. Numbers in the graph represent the compounds in Table 1.

drawal from the manganese atom to the tin atom,[22] while an increase in the ^{119}Sn-isomer shift implies sσ-electron deposit on the tin atom. This trend may also suggest an electron transfer from the manganese to the tin atom through the σ-bond.

In the series of $(CH_3)_{3-x}X_xSn\text{-}Mn(CO)_5$, there are linear decreases in the $^1H(CH_3)$-chemical shift and in the coupling constant, $J(^{119}Sn\text{-}^1H(CH_3))$, with an increase in the ^{119}Sn-isomer shift, as is shown in Fig. 4.

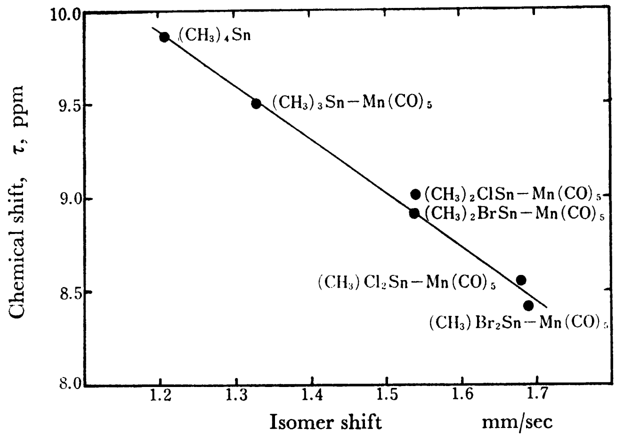


Fig. 4(a). The relationship between ^{1}H-chemical shift and ^{119}Sn-isomer shift.

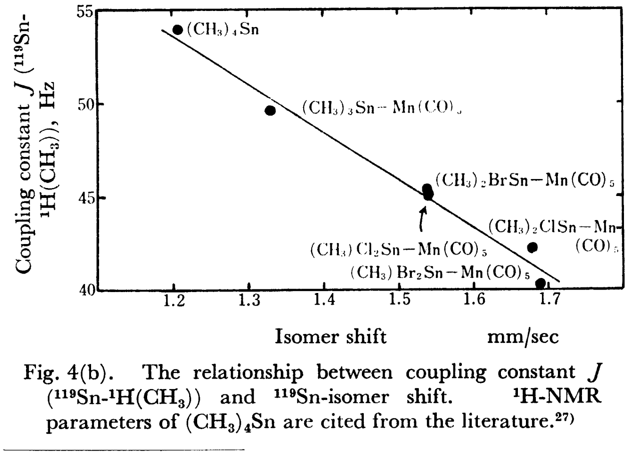


Fig. 4(b). The relationship between coupling constant J ($^{119}Sn\text{-}^1H(CH_3)$) and ^{119}Sn-isomer shift. ^{1}H-NMR parameters of $(CH_3)_4Sn$ are cited from the literature.[27]

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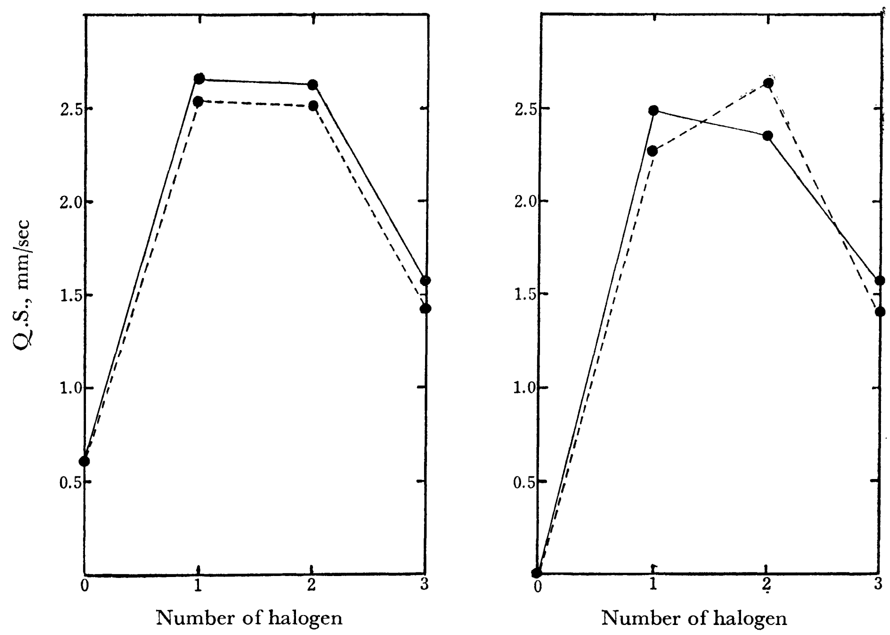
[22] The detailed discussion in context with CO stretching vibrations will be published elsewhere.

[27] N. Flitcroft and H. D. Kaesz, *J. Amer. Chem. Soc.*, **85**, 1377 (1963).



(a) (b)

Fig. 5. Relationships between quadrupole splitting and number of halogen on tin atom.

(a). ●—● represents $(CH_3)_{3-x}Cl_xSn-Mn(CO)_5$, ●···● $(CH_3)_{3-x}Br_xSn-Mn(CO)_5$ respectively.

(b). ●—● represents $Ph_{3-x}Cl_xSn-Mn(CO)_5$, ●···● $Ph_{3-x}Br_xSn-Mn(CO)_5$ respectively.

Decreases in the coupling constant and increases in the isomer shift with the decrease in the number of methyl group attached to the tin atom may be expected by assuming a higher *p*-character in the tin-halogen bond and a higher *s*-character in the tin-manganese bond than in the other tin-ligand bond.[23,24] The lower coupling constant, $J(^{119}Sn\text{-}^1H(CH_3))$, in $(CH_3)_3Sn-Mn(CO)_5$ than in $(CH_3)_4Sn$ also indicates that the 5s electron of tin atom is much more localized in the tin-manganese bond than in the tin-carbon bond; *i.e.*, the tin-manganese bond prefers the sσ-character whereas the tin-carbon bond prefers the pσ-character.[25]

The quadrupole splitting of the Mössbauer spectra reflects the electric-field gradient at the tin nucleus. Although the intermolecular interactions might not be negligible in some cases, the dominant origin of the electric-field gradient may be ascribed to the intramolecular bonding around the tin atom as a first approximation. It is found, from the data shown in Fig. 5, that $R_2XSn-Mn(CO)_5$ and $RX_2Sn-Mn(CO)_5$ give the same order of quadrupole splitting values except in the cases of $Ph_2BrSn-Mn(CO)_5$ and $PhBr_2Sn-Mn(CO)_5$, and that $R_{3-x}Br_xSn-Mn(CO)_5$ gives a lower quadrupole splitting value than the analogous $R_{3-x}Cl_xSn-Mn(CO)_5$, while R is the same in both the compounds, again with the exception of $PhBr_2$ Sn–$Mn(CO)_5$. Intermolecular interactions might not be negligible in this compound. The general trend for the quadrupole splitting values to be higher for chloride compounds than for bromide suggests that the *p*-electron imbalance in the 5p-orbital of the tin atom is greater in $R_{3-x}Cl_x$-$Sn-Mn(CO)_5$ than in $R_{3-x}Br_xSn-Mn(CO)_5$. As has been mentioned in the previous section, it was found that the *p*-character is highest in the tin-halogen bond and lowest in the tin-manganese bond. This p-electron imbalance in each tin-ligand bond may be considered to be the main origin of the quadrupole splitting. As may be seen in Fig. 6, $Ph_3Sn-Mn(CO)_5$ shows non-resolved quadrupole splitting, whereas $(CH_3)_3Sn-Mn(CO)_5$ gives a clearly-resolved spectrum. In general, quadrupole splitting is larger when R is CH_3 than when R is C_6H_5. Cordey-Hayes *et al.*[26] and Stöckler and Sano[3] pointed out that the phenyl groups are more effective in delocalizing π-electrons and, hence, in reducing the magnitude of the quadrupole splitting in the series of $Ph_{4-x}X_xSn$ compounds. Parish and Platt interpreted the fact that the quadrupole splitting is smaller in $Ph_{4-x}X_xSn$ than in $(CH_3)_{4-x}X_xSn$ compounds by assuming a higher electron-withdrawing ability of the phenyl group.[5] However, the ^{119}Sn-isomer shift and the ^{55}Mn-chemical shift data indicate that the $Mn(CO)_5$ group has a stronger σ-electron-donating ability either than the methyl or the phenyl group. The results led us to conclude that the phenyl group reduces the magnitude of quadrupole splitting

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[23] H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960); *Chem. Rev.*, **61**, 275 (1961); *J. Inorg. Nucl. Chem.*, **19**, 43 (1961).

[24] J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

[25] It has been reported that the *p*-character in tin-halogen bond is larger than in tin-carbon bond in $(CH_3)_{4-x}X_xSn$ compounds. J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961); M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, **3**, 1157 (1964); E. V. van der Berghe and G. P. van der Kelen, *Ber. Bunsenges. Phys. Chem.*, **68**, 652 (1964).

[26] M. Cordey-Hayes, R. D. Peacock, and M. Vucelic, *J. Inorg. Nucl. Chem.*, **29**, 1177 (1967).

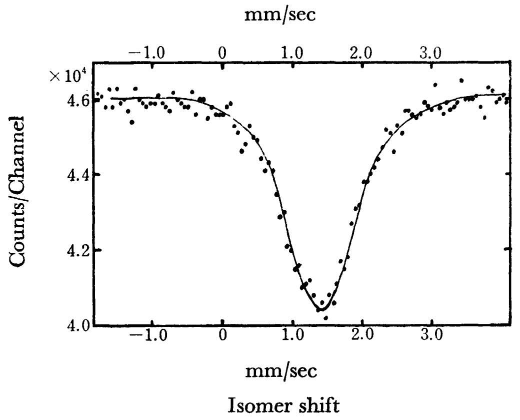

Fig. 6(a). A ^{119}Sn-Mössbauer spectrum of $Ph_3Sn-Mn(CO)_5$.

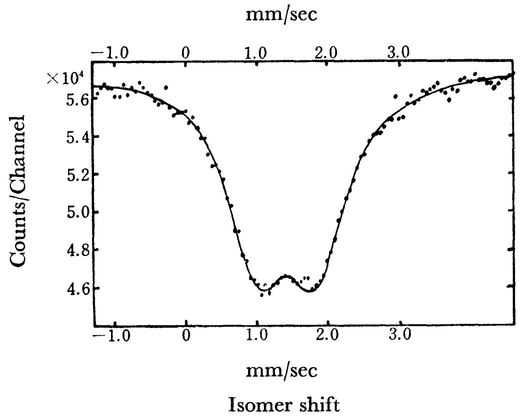

Fig. 6(b). A ^{119}Sn-Mössbauer spectrum of $(CH_3)_3Sn-Mn(CO)_5$.

more than the methyl group, whether X is an electronegative or an electropositive group, since the π-backdonation from $Mn(CO)_5$ to Sn in $Ph_3Sn-Mn(CO)_5$ is found not to be stronger than that in $(CH_3)_3Sn-Mn(CO)_5$ from the findings on the ^{55}Mn-NMR linewidth.[17] A plausible explanation is the ability of the phenyl group to deposit or withdraw π-electrons through a mesomeric effect and thereby cause a delocalization of π-electrons.

Conclusion

In compounds of the $R_{3-x}X_xSn-Mn(CO)_5$ type, where R is (CH_3) or (C_6H_5) and where X is Cl or Br, ^{119}Sn, ^{55}Mn, and ^{1}H were used as probes to derive information as to the electronic configuration. All the results of the ^{119}Sn-isomer shift, the ^{55}Mn-chemical shift, the $^1H(CH_3)$-chemical shift, and the $J(^{119}Sn-^1H(CH_3))$ coupling constant indicate that the $Mn(CO)_5$ group is a stronger electron donor than the methyl, phenyl, or halogen group and that the tin-manganese bond prefers the sσ-character, whereas the tin-halogen bond prefers the pσ-character. The σ-electron transfer from the manganese to the tin atom increases with the successive replacement of the organic groups on tin atom by the halogen atoms. The relationship between the ^{55}Mn-chemical shift and the ^{119}Sn-Mössbauer isomer shift shows that the ^{55}Mn-chemical shift values (from $KMnO_4$ standard) become smaller when the degree of $Mn \xrightarrow{\sigma} Sn$-type σ-electron transfer increases. In general, the phenyl group reduces the magnitude of the quadrupole splitting more than the methyl group, as has been observed in the series of the $R_{4-x}X_xSn$ compound. This behavior can be interpreted as being due to the mesomeric effect of the phenyl group through the π-bond between tin and ligand atoms.

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