A Long-range Effect of Weaker π-Accepting Ligands, $M(C_6H_5)_3$ (M=P, As, and Sb), on the ^{119}Sn-Mössbauer Quadrupole Splitting in the $R_3Sn\text{-}Mn(CO)_4M(C_6H_5)_3$ Compounds

Satoru ONAKA and Hirotoshi SANO*,**

Department of Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya
**Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo*

(Received December 10, 1971)

We have recently reported that $(C_6H_5)_{3-x}X_xSn\text{–}Mn(CO)_5$ compounds show a smaller quadrupole splitting than their methyl analogues, $(CH_3)_{3-x}X_xSn\text{–}Mn(CO)_5$ (X=Cl and Br).[1] This finding has been interpreted in terms of the π-delocalizing effect of the phenyl group in $(C_6H_5)_{3-x}X_xSn\text{–}Mn(CO)_5$. It has also been pointed out that the π-interaction between tin and manganese atoms may affect the quadrupole splitting (Q.S.) in the ^{119}Sn-Mössbauer spectra of these compounds. The present studies were undertaken in order to provide evidence of the π-delocalizing effect of the phenyl group upon the Q. S. and to elucidate the π-interaction between tin and manganese atoms. For this purpose, the effect of the substitution of the CO group in $R_3Sn\text{–}Mn(CO)_5$ with a weaker π-accepting ligand L (L= $P(C_6H_5)_3$, $As(C_6H_5)_3$, or $Sb(C_6H_5)_3$) was studied.[2,3]

$(C_6H_5)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$ and $(C_6H_5)_3Sn\text{–}Mn(CO)_4As(C_6H_5)_3$ were prepared by the method of Gorsich.[4] The other compounds not found in the literature were prepared by the direct replacement of CO with a ligand, L. The ^{119}Sn–Mössbauer spectra were measured against a barium stannate source moving in a constant acceleration mode at room temperature. The sample was used as an absorber and was kept at 79°K in a cryostat.

As is shown in Table 1, such a replacement causes no appreciable change in the isomer shift (I.S.), but it does cause a remarkable decrease in the Q.S. in methyl compounds; *i.e.*, $(CH_3)_3Sn\text{–}Mn(CO)_5$ gives a clearly-resolved quadrupole split spectrum, whereas $(CH_3)_3Sn\text{–}Mn(CO)_4L$ gives a non-resolved spectrum, as is illustrated in Fig. 1. These results mean that the σ-characters of the Sn–Mn bond are not affected enough to be detected by the Mössbauer spectroscopy. It seems reasonable to conclude that the origin of the change in the electron distribution around the tin nucleus for methyl derivatives is due to the change in the π-interaction between tin and manganese atoms.[5]

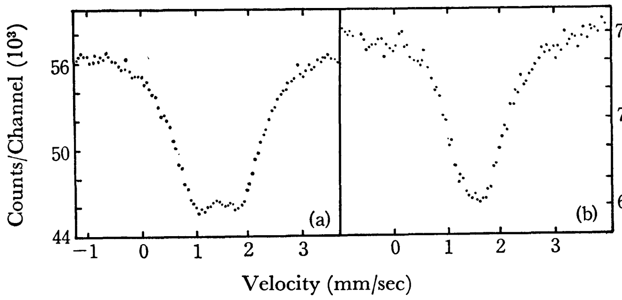

Fig. 1. Mössbaure spectra of (a) $(CH_3)_3Sn\text{–}Mn(CO)_5$ and (b) $(CH_3)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$.

IR spectroscopic study shows that these compounds have two peaks in the CO stretching region. The IR data and the results of the single crystal X-ray diffraction analysis for $(C_6H_5)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$ indicate a *trans* configuration for all the substituted compounds; *i.e.*, the ligand, L, is coordinated to the manganese atom at the *trans* position with regard to the tin atom. In this *trans* configuration, the tin atom is supposed to compete with the ligand, L, for the d_π-electrons of the manganese atom. As the π-accepting ability of the ligand, L, is weaker than that of the substituted CO,[2,3] the d_π-electrons of manganese atom are forced to enter both the vacant 5*d* orbitals of the tin atom and the CO π-antibonding orbitals.[6] Thus, the π-accepting ability of the ligand, L, influences the efg around the tin nucleus through the π-electrons of the manganese atom. Such a long-range effect through the π-interaction should not be overlooked, although it has not yet been reported.[7]

The reason why the zero quadrupole splitting in $(C_6H_5)_3Sn\text{–}Mn(CO)_5$ is not affected by the replacement of CO with L may well be explained in terms of the predominant π-delocalizing effect of the phenyl groups attached to the tin atom.[1]

TABLE 1. ^{119}Sn-MÖSSBAUER PARAMETERS

Compound	I.S.[a] (mm/sec)	Q.S. (mm/sec)
$(CH_3)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$	1.27	~0
$(CH_3)_3Sn\text{–}Mn(CO)_4As(C_6H_5)_3$	1.28	~0
$(CH_3)_3Sn\text{–}Mn(CO)_5$	1.33	0.61
$(C_6H_5)_3Sn\text{–}Mn(CO)_4(C_6H_5)_3$	1.43	0
$(C_6H_5)_3Sn\text{–}Mn(CO)_4As(C_6H_5)_3$	1.38	0
$(C_6H_5)_3Sn\text{–}Mn(CO)_4Sb(C_6H_5)_3$	1.40	0
$(C_6H_5)_3Sn\text{–}Mn(CO)_5$	1.41	0

a) All the isomer shifts are with respect to $BaSnO_3$ at room temperature.

** Present address: Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku Tokyo.

1) S. Onaka, Y. Sasaki, and H. Sano, This Bulletin, **44**, 726 (1971).

2) S. Onaka, *ibid.*, **44**, 2135 (1971).

3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Chapter VII, John Wiley & Sons, New York (1967).

4) R. D. Gorsich, *J. Amer. Chem. Soc.*, **84**, 2468 (1962).

5) X-ray analyses for $(C_6H_5)_3Sn\text{–}Mn(CO)_5$, $(CH_3)_3Sn\text{–}Mn(CO)_5$, and $(C_6H_5)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$ indicate that the bond angles around the tin atom of $(CH_3)_3Sn\text{–}Mn(CO)_4L$ are not greatly distorted from the tetrahedral angle through the replacement; H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22**, 822 (1967); R. F. Bryan, *J. Chem. Soc.*, *A*, **1967**, 172; *ibid.*, **1968**, 696.

6) The increase in the π-characters between the manganese atom and the remaining CO is substantiated by their IR spectra, since the corresponding absorption peaks of ν(CO) shift to lower wave numbers in the substitution of *trans* CO.[2,3]

7) We have previously reported a similar long-range effect in ^{55}Mn-NMR for $Mn(CO)_5SnL_3$. S. Onaka, T. Miyamoto, and Y. Sasaki, This Bulletin, **44**, 1851 (1971).