October, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 3085—3089 (1986)

# $^{121}Sb$ Mössbauer and $^{1}H$ and $^{13}C$ NMR Spectroscopic Studies of a Series of Organoantimony(V) Compounds, $R_3SbX_2$

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(Received April 26, 1986)

The $^{121}Sb$ Mössbauer spectroscopic and the $^{1}H$ and $^{13}C$ NMR nuclear magnetic resonance studies have been performed for a series of organoantimony(V) compounds: $R_3SbX_2$ (R=$CH_3$, $C_6H_5$, $p$-$CH_3C_6H_4$; X=F, Cl, Br, I). For the trimethylantimony dihalides, the isomer shifts and quadrupole coupling constants of the $^{121}Sb$ Mössbauer spectra indicated that the withdrawal of the bonding electrons from the antimony atom along Sb–X increased, as the electronegativity of the halogen increased. The chemical shifts of the $^{1}H$ and $^{13}C$ NMR spectra showed that the electron population around the methyl group increased with increasing electronegativity of halogen. For phenyl and $p$-tolyl derivatives, both $^{121}Sb$ Mössbauer and $^{13}C$ NMR data showed a trend similar to the methyl compounds. The results suggest that the electron cloud around the antimony atom spreads, with an increase in the electronegativity of the halogen, not only toward the halogen atoms but also toward the plane perpendicular to the bonding direction with the halogen atoms.

Mössbauer spectroscopy is a sensitive tool for studying the effect of the chemical environment on the electron density at and around a Mössbauer atom. Antimony contains 57.25% of the naturally occuring isotope $^{121}Sb$. The nuclear radius factor, $\Delta R/R$, of $^{121}Sb$ is considerably large (about $-1\times10^{-3}$).[1] Hence, a large change in the isomer shift can be expected for varieties of antimony compounds, although a large natural line width of 2.11 mm s$^{-1}$ will result in an inaccuracy in the evaluation of the data.

If Mössbauer spectroscopy is used in combination with other spectroscopies, it is possible to elucidate how an electron is redistributed throughout a molecule when some ligands are varied.[2–5] For example, the effect of various ligands on the electron distribution, especially around tin atoms in the molecules of $R_{3-x}X_xSn$-$Mn(CO)_5$ (R=$CH_3$, $C_6H_5$; X=Cl, Br), was successfully studied by combining $^{119}Sn$ Mössbauer spectroscopy and $^{1}H$ and $^{55}Mn$ NMR.[3]

For trimethyl- and triphenylantimony dihalides, several structural studies by the X-ray diffraction method[6,7] and infrared and Raman spectroscopy[8–12] have been reported. $^{121}Sb$ Mössbauer spectra have also been reported for some of trimethyl- and triphenylantimony dihalides.[13–15]

In the present work, we have examined the correlation between the electronic state at antimony atoms, deduced from the isomer shifts and the nuclear quadrupole coupling constants of $^{121}Sb$ Mössbauer spectra, and the electron distributions of the ligands, revealed by their chemical shifts in $^{1}H$ and $^{13}C$ NMR spectra for a series of organoantimony(V) compounds, trimethylantimony dihalides $(CH_3)_3SbX_2$ (X=F, Cl, Br, I), triphenylantimony dihalides $(C_6H_5)_3SbX_2$ (X=Cl, Br, I), and tri-$p$-tolylantimony dihalides $(p$-$CH_3C_6H_4)_3SbX_2$ (X=Cl, Br, I). Mössbauer spectra were measured at 20 K and analyzed by using the transmission integral in order to take into account the effect of the thickness of the absorber on the spectra.

## Experimental

**Preparation of Compounds.** All the compounds were prepared by methods described in the literature[8,16,17] or analogous methods. For example, tri-$p$-tolylantimony dichloride was synthesized by the following method. Antimony trichloride (25 g) dissolved in 250 ml of dry benzene was added slowly to the Grignard reagent prepared from 9.5 g magnesium and 72 g $p$-bromotoluene dissolved in 250 ml of absolute ether, and the mixture was boiled for thirty hours. The filtrate was distilled under reduced pressure, and the soluble residue was removed by extraction with small quantities of ethanol. The tri-$p$-tolylstibine was further purified by crystallization from carbon tetrachloride (yield; 20.5 g, 47.3%). Tri-$p$-tolylstibine (5 g), dissolved in 30 ml of carbon tetrachloride, was treated with chlorine until the solution became yellow. Most of the solvent and the excess chlorine were then removed using a steam bath. The tri-$p$-tolylantimony dichloride was separated from the cold concentrated solution, and recrystallized from carbon tetrachloride (yield; 3.2 g, 54.2%).

The purity of the compounds studied in the present work was checked by elemental analyses of carbon and hydrogen, and by IR and/or NMR.

**Mössbauer Spectra.** The $^{121}Sb$ Mössbauer absorption spectra were obtained using $\simeq$440 $\mu$Ci $Ca^{121m}SnO_3$ source moving in a constant acceleration mode. The source and the absorber containing 13—25 mg cm$^{-2}$ of Sb were both kept at 20 K in a cryostat[18] and the 37.14 keV resonance $\gamma$-rays were detected by counting the escape peak in a Xe–$CO_2$ proportional counter. Generally, the measurement was continued until 1—3$\times10^4$ counts/channel was achieved. The velocity scale was calibrated by using a laser interferometer.

The spectra were analyzed by the program of least-squares fitting of transmission integrals,[19–22] edited by L. H. Bowen.[23] The value of 1.34 was used as a fixed parameter for $Q(7/2)/Q(5/2)$ in analyses.[24]

**$^{1}H$ and $^{13}C$ NMR Spectra.** The $^{1}H$ and $^{13}C$ NMR spectra were observed at room temperature for the chloroform-$d$ solution containing 1% tetramethylsilane (TMS) as the internal standard. A PMX 60SI spectrometer and a JNM-FX60, Fourier transform spectrometer were used for the measurement of $^{1}H$ and $^{13}C$ NMR, respectively.

## Results and Discussion

The observed $^{121}$Sb Mössbauer spectra for the trimethylantimony dihalides are shown in Fig. 1. The Mössbauer parameters obtained in the present work for a series of compounds are summarized in Table 1. The absolute value of the isomer shift (IS) decreases and that of the quadrupole coupling constant ($e^2q_zQ$) increases as the electronegativity of the halogen increases for all the trimethyl, triphenyl, and tri-*p*-tolyl compounds.

On the assumption that the contribution of the core electrons to the electron density at the nucleus of antimony is, as a first approximation, the same for all the compounds studied and that the shielding effect on the 5s electrons by 5d electrons is considerably smaller than that by the 5p electrons, 5s and 5p electrons can be considered mainly responsible for the observed Mössbauer parameters. As the absolute value of the IS is proportional to the electron density at the antimony nucleus, the trend of the IS shows that the s electron density decreases as the electronegativity of the ligand halogen atom increases. This fact implies the withdrawal of s electrons from the antimony atom along Sb–X.

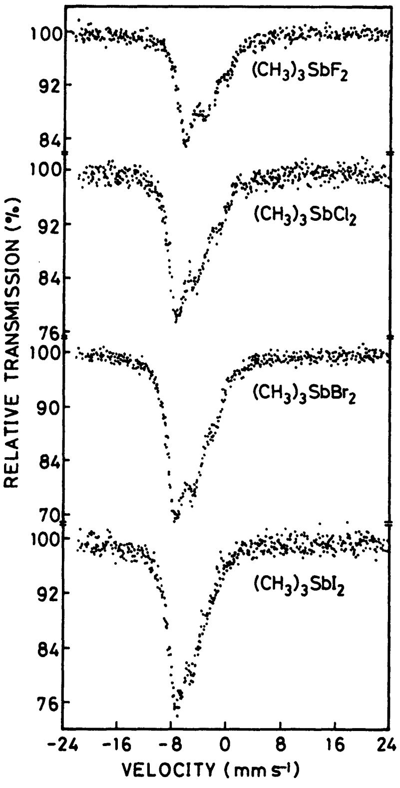


Fig. 1. $^{121}$Sb Mössbauer spectra of $(CH_3)_3SbX_2$ (X=F, Cl, Br, I) against a Ca$^{121m}$SnO$_3$ source at 20 K.

All the compounds investigated are found to have large negative $e^2q_zQ$, indicating the main component of the electric field gradient, $eq_z$, is positive since the quadrupole moment, $eQ$, of the $^{121}$Sb nucleus is negative.

X-Ray structural studies for $R_3SbX_2$ ($R=CH_3$, $C_6H_5$; X=Cl, Br, I) revealed that the trigonal bipyramidally coordinated antimony atom has two halogen atoms occupying the apical positions along the *z*-axis and three organic ligands situating in the *x*–*y* plane,[6,7] and the sp$^3$d hybrid is expected.[15] Neglecting 5d orbital contributions, the electric field gradient, $eq_z$, due to the asymmetric p electrons and the asymmetric factor, $\eta$, can be written in general as

$$eq_z = C\{-N_{p_z}+1/2(N_{p_x}+N_{p_y})\}$$

and

$$\eta = 3(N_{p_x}-N_{p_y})/\{-2N_{p_z}+(N_{p_x}+N_{p_y})\},$$

where $N_{p_i}$ with $i=x$, $y$, $z$ represents the orbital population along the three directions and $C$ is a constant with the positive sign. This axial symmetry allows us to put $N_{p_x}=N_{p_y}$ and $\eta=0$. The observed positive $eq_z$ means that the p electron density along the *x* and *y* directions is greater than that along the *z*-axis. The trend that the electric field gradient at the antimony nuclear site increases as the electronegativity of the halogen atoms increases suggests that the electrons in the $p_z$ orbital is withdrawn toward the halogen atom along Sb–X.

Two $^{121}$Sb Mössbauer parameters, IS and $e^2q_zQ$, both show that the electron attraction by the halogen

Table 1. $^{121}$Sb Mössbauer Parameters for $R_3SbX_2$ Compounds

| Compound | IS/mm s$^{-1}$[a] | $e^2q_zQ$/mm s$^{-1}$[b] | $\Gamma_{exp}$/mm s$^{-1}$ |
|---|---|---|---|
| $(CH_3)_3SbF_2$ | −4.90±0.03 | −24.1±0.3 | 2.53±0.04 |
| $(CH_3)_3SbCl_2$ | −6.01±0.04 | −23.1±0.3 | 2.49±0.05 |
| $(CH_3)_3SbBr_2$ | −6.23±0.02 | −21.6±0.1 | 2.29±0.04 |
| $(CH_3)_3SbI_2$ | −6.44±0.03 | −18.3±0.3 | 2.42±0.01 |
| $(C_6H_5)_3SbCl_2$ | −6.00±0.02 | −21.1±0.2 | 2.29±0.04 |
| $(C_6H_5)_3SbBr_2$ | −6.22±0.02 | −19.4±0.2 | 2.32±0.01 |
| $(C_6H_5)_3SbI_2$ | −6.42±0.03 | −17.2±0.3 | 2.26±0.03 |
| $(p\text{-}CH_3C_6H_4)_3SbCl_2$ | −5.84±0.05 | −20.9±0.5 | 2.16±0.07 |
| $(p\text{-}CH_3C_6H_4)_3SbBr_2$ | −6.07±0.03 | −19.7±0.3 | 2.27±0.07 |
| $(p\text{-}CH_3C_6H_4)_3SbI_2$ | −6.14±0.07 | −17.2±0.7 | 2.68±0.02 |

a) Relative to a Ca$^{121m}$SnO$_3$ source. b) $Q(7/2)/Q(5/2)=1.34$ was used as a fixed parameter and the listed values were estimated for the $Q(5/2)$ value.

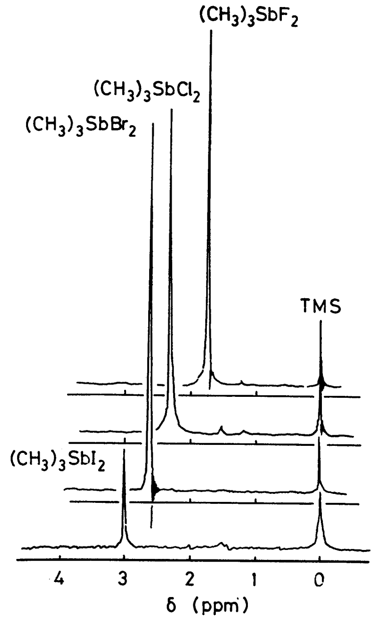


Fig. 2. $^{1}$H NMR spectra of $(CH_3)_3SbX_2$ (X=F, Cl, Br, I) in $CDCl_3$ at room temperature. Tetramethylsilane (TMS) was used as the internal standard.

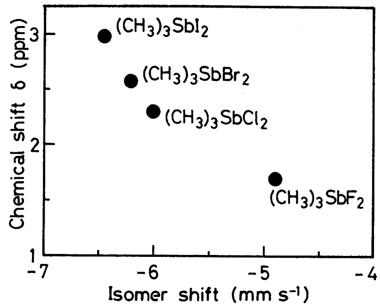


Fig. 3. Relationship between $^{121}$Sb Mössbauer isomer shift (relative to a $Ca^{121m}SnO_3$ source) and $^{1}$H NMR chemical shift (with respect to TMS).

Table 2. $^{1}$H and $^{13}$C NMR Parameters for $(CH_3)_3SbX_2$ Compounds

| Compound | $^{1}$H chemical shift | $^{13}$C chemical shift |
|---|---|---|
| | ppm[a] | ppm[a] |
| $(CH_3)_3SbF_2$ | 1.70 | 9.3 |
| $(CH_3)_3SbCl_2$ | 2.30 | 22.9 |
| $(CH_3)_3SbBr_2$ | 2.57 | 26.5 |
| $(CH_3)_3SbI_2$ | 2.98 | 31.9 |

a) Relative to $(CH_3)_4Si$ (TMS).

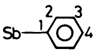
increases, as the electronegativity difference between the halogen and antimony increases.

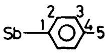
It is further noted that the absolute values of the IS decrease slightly for the same halogen atom in the order of $(CH_3)_3SbX_2$, $(C_6H_5)_3SbX_2$, and $(p\text{-}CH_3C_6H_4)_3SbX_2$ as shown in Table 1, when we compare the effects of ligands in the $x$–$y$ plane. The electron releasing ability of these substituents is known to be in the order of methyl>*p*-tolyl>phenyl group. In fact, for the *p*-tolyl and phenyl derivatives, the electron density of the carbon bonded to the antimony atom was found to increase with this sequence, which will be shown later ($^{13}$C NMR data in Table 3). In the foregoing discussion, the shielding effects of the 5s electrons by 5d electrons were ignored in comparison to those due to the 5p electrons. However, as a minor effect, the s electron density at the $^{121}$Sb nuclear site will slightly decrease with an increase of the density on the 5d orbitals. In the case of $(p\text{-}CH_3C_6H_4)_3SbX_2$, the electron-donating methyl group bonded to the phenyl ring may cause the $\pi$-electron density of the carbon bonded to the antimony higher. Although the X-ray diffraction data have not yet been available for the *p*-tolyl derivative, the $\pi$-orbital may interact with the vacant $5d_{xz}$ and $5d_{yz}$ orbitals of antimony. This interaction may enhance the shielding effects, resulting in the decrease of 5s electron density at the $^{121}$Sb nuclear site. This will be one of the possible reasons for the observed Mössbauer parameters.

In order to examine in more detail the electron distribution around antimony, we compared the $^{1}$H and $^{13}$C NMR data with the $^{121}$Sb Mössbauer data. The $^{1}$H NMR spectra of trimethylantimony dihalides are shown in Fig. 2. In Fig. 3 is illustrated the relationship between the $^{121}$Sb Mössbauer isomer shift and $^{1}$H NMR chemical shift; $^{1}$H chemical shift smoothly decreases as the absolute value of the isomer shift decreases. The values of the chemical shift, $\delta$, of $^{1}$H and $^{13}$C NMR for trimethylantimony dihalides are listed in Table 2. Both $^{1}$H and $^{13}$C NMR chemical shifts are observed at higher fields as the electronegativity of the halogen coordinated to the antimony increases. This implies that the electron population becomes larger around the methyl group when the more electronegative halogen is attached to the antimony atom. The s electron density at the antimony itself decreases as shown by the Mössbauer isomer shift. The present NMR data are consistent with those on the streching force constant ($k$) of antimony-carbon atoms obtained for $(CH_3)_3SbX_2$ (X=F, Cl, Br) by far-infrared spectroscopy ($k$ decreases in the order of X=F, Cl, Br).[11] The present observation is, however, contrary to the one reported on methyl halides $CH_3X$, where the chemical shifts of $^{1}$H NMR are observed at lower fields as the electronegativity of the halogen increases.[25]

The values for $^{13}$C chemical shift of the triphenyl and tri-*p*-tolylantimony dihalides are summarized in Table 3. In the case of triphenyl and tri-*p*-tolylantimony dihalides, the $\delta$ value for the carbon atom coordinated to the antimony atom shifts toward a higher field as the electronegativity of the halogen increases, indicating that the electron population increases at the carbon atom coordinated to the antimony atom. This trend agrees with the case of trimethylantimony dihalides. However, Table 3 also shows that the $\delta$ values of the *o*- and *p*-carbon atoms shift toward lower fields although

Table 3. $^{13}$C NMR Parameters for $(C_6H_5)_3SbX_2$ and $(p\text{-}CH_3C_6H_4)_3SbX_2$ Compounds





| Compound | Chemical shift/ppm[a] | | | | |
|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | C-4 | C-5 |
| $(C_6H_5)_3SbCl_2$ | 140.0 | 134.2 | 129.6 | 131.8 | — |
| $(C_6H_5)_3SbBr_2$ | 141.0 | 133.6 | 129.5 | 131.6 | — |
| $(C_6H_5)_3SbI_2$ | 141.3 | 133.2 | 129.5 | 131.4 | — |
| $(p\text{-}CH_3C_6H_4)_3SbCl_2$ | 136.6 | 133.9 | 130.1 | 142.1 | 21.4 |
| $(p\text{-}CH_3C_6H_4)_3SbBr_2$ | 137.7 | 133.5 | 130.1 | 142.0 | 21.4 |
| $(p\text{-}CH_3C_6H_4)_3SbI_2$ | 138.0 | 133.1 | 130.1 | 141.8 | 21.5 |

a) Relative to $(CH_3)_4Si$ (TMS).

the $\delta$ values for the *m*-carbon stays constant. This implies that the $\pi$-electron density is withdrawn from the phenyl or *p*-tolyl group to the antimony, indicating the electrophilic nature of the antimony atom.

These results may imply that the electron cloud around the antimony atom spreads in the $x$–$y$ plane as well as in the $z$ direction with an increase in the electronegativity of the halogen atom. Therefore, the electron density on the carbon coordinated to the antimony might be increased.

## Conclusion

In a series of organoantimony(V) compounds $R_3SbX_2$ ($R=CH_3$, $C_6H_5$, $p\text{-}CH_3C_6H_5$; $X=F$, Cl, Br, I), the $^{121}$Sb Mössbauer spectra and $^1$H and $^{13}$C NMR spectra were measured. Interesting information concerning the electron distribution around the antimony atom was obtained.

As the electronegativity of the halogen occupying the apical position along the $z$-axis in the trigonal bipyramidal structure increases, (1) the $^{121}$Sb Mössbauer data show an increasing withdrawal of the electron density from the antimony atom to the halogen atom, and (2) the $^1$H and $^{13}$C NMR chemical shifts show the increase of the electron population at the methyl group in trimethylantimony dihalides and on the carbon coordinated to the antimony of the aromatic group in the triphenyl and tri-*p*-tolylantimony dihalides. These facts suggest that the cloud of the electrons around the antimony atom spread along the $x$ and $y$ directions with an increasing tendency for the withdrawal of the electron density from the antimony along the $z$-axis.

The authors gratefully acknowledge the cooperation of Drs. Yasuyuki Miyazawa, Haruo Matsuyama, and Masato Yoshida, and Prof. Dr. Michio Kobayashi of Tokyo Metropolitan University in the measurements of the $^1$H and $^{13}$C NMR spectra. We would also like to thank Dr. Masashi Takahashi of Toho University for measurements of the $^{121}$Sb Mössbauer spectra. The authors are also indebted to Prof. Dr. Lawrence H. Bowen at North Carolina State University for a least-squares fitting program of transmission integrals.

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