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On the Behavior of the Mixture of Trimethylstibine Sulfide and Tin(IV) Halides in Solution

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In the previous papers[1,2] we have reported that the complexes, $R_2SnX_2 \cdot 2(CH_3)_3SbS$ ($R = CH_3$ or C_2H_5; $X = Cl$ or Br), change completely into three species with the exchange of the anionic ligands in $CHCl_3$ or CH_2Cl_2 as shown in (1).

$$R_2SnX_2 \cdot 2(CH_3)_3SbS \rightarrow (CH_3)_3SbS + (CH_3)_3SbX_2 + \tfrac{1}{3}(R_2SnS)_3 \qquad (1)$$

This paper reports additional studies of these particular exchange reactions in $CHCl_3$ or CH_2Cl_2 with the mixtures of $(CH_3)_3SbS$ and R_3SnCl ($R = CH_3$ and C_6H_5) or $(C_6H_5)_2SnCl_2$, although we have not been able to isolate the complexes between the stibine sulfide and the tin chlorides.[2]

Experimental

The materials used in the present experiments and the experimental methods were described in the previous paper.[2]

Results and Discussion

The IR spectra of the mixtures of $(CH_3)_3SbS$ and $(CH_3)_3SnCl$ in various ratios were measured in solution and the relevant IR frequencies of a mixture of $(CH_3)_3SbS$ and $2(CH_3)_3SnCl$ in $CHCl_3$ are given in Table 1.

The spectrum can plausibly be interpreted as a superposition of the four compounds observed independently in $CHCl_3$; $(CH_3)_3SbS$,[2] $(CH_3)_3SnCl$, $(CH_3)_3SbCl_2$[2] and $[(CH_3)_3Sn]_2S$.

The NMR spectrum shown in Fig. 1 also supports this result.

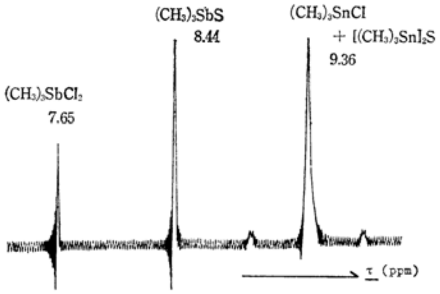

Fig. 1. The NMR spectrum of the mixture of $2(CH_3)_3SnCl$ and $(CH_3)_3SbS$ in $CHCl_3$ at 60 Mc/sec at 20°C.

For the antimony compounds the corresponding

Table 1. The IR frequenciens of the mixture of $(CH_3)_3SnCl$ and $(CH_3)_3SbS$ in $CHCl_3$ (600—400 cm^{-1} region)

$2(CH_3)_3SnCl$ $+(CH_3)_3SbS$	$[(CH_3)_3Sn]_2S$	$(CH_3)_3SnCl$	$(CH_3)_3SbS$[2]	$(CH_3)_3SbCl_2$[2]	Possible assignment
572 vw				572 m	Sb–C deg. str.
—*			551 m		Sb–C deg. str.
545 s		545 s			Sn–C deg. str.
532 m	533 s		531 m		Sb–C sym. str. +Sn–C deg. str.
515 w		514 w			Sn–C sym. str.
509 w(sh).	508 m				Sn–C sym. str.
433 m			433 m		Sb–S str.

* Masked by the strong band at 545 cm^{-1}.

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[1] M. Shindo and R. Okawara, *Inorg. Nucl. Chem. Letters*, **3**, 75 (1967).

[2] M. Shindo, Y. Matsumura and R. Okawara, *J. Organometal Chem.*, **11**, 299 (1968).

two signals were observed. However, the tin compounds showed only one signal at 9.36 ppm. This signal is due to the rapid exchange of chlorine-sulfur atoms or methyl groups between $(CH_3)_3SnCl$ and $[(CH_3)_3Sn]_2S$, for the signal moves to higher field to approach that of $[(CH_3)_3Sn]_2S$ with decreasing ratio of $(CH_3)_3SnCl$ to $[(CH_3)_3Sn]_2S$. The same IR and NMR results were obtained in the case of a mixture of $(CH_3)_3SbCl_2$ and $[(CH_3)_3Sn]_2S$.

From these findings it is clear that the four species exist in equilibrium as shown in (2).

$$2(CH_3)_3SnCl + (CH_3)_3SbS \rightleftarrows (CH_3)_3SbCl_2 + [(CH_3)_3Sn]_2S \qquad (2)$$

The molar concentrations of $(CH_3)_3SnCl$ and $[(CH_3)_3Sn]_2S$ can be determined from the intensity ratio of methyl protons of $(CH_3)_3SbS$ to those of $(CH_3)_3SbCl_2$ and Eq. (2). From these results the equilibrium constant, $K = [Me_3SbCl_2][(Me_3Sn)_2S]/[Me_3SnCl]^2[Me_3SbS]$, of Eq. (2) was calculated to be 0.14 (l/mol) at 20°C. Similarly, in cases of $(C_6H_5)_3SnCl$ and $(C_6H_5)_2SnCl_2$, the equilibrium constants are $80\,(l/\text{mol})$ and $\infty\,(l/\text{mol})^{2/3}$, respectively. It can be understood that in the case of $(C_6H_5)_2SnCl_2$ the equilibrium goes, just in the cases of Eq. (1), too much toward the right side. From these it can be concluded that, in general, the equilibrium constant increases as the electron acceptor properties of the tin com- pounds increase.

$$(CH_3)_3SnCl < (C_6H_5)_3SnCl < (CH_3)_2SnCl_2 \sim (C_6H_5)_2SnCl_2$$