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ORGANOMETALLIC COMPLEXES CONTAINING ANTIMONY AND ALUMINUM

I. COMPLEX FORMATION OF ALKYLANTIMONY COMPOUNDS WITH ALUMINUM COMPOUNDS, $AlEt_nCl_{3-n}$

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INTRODUCTION

During the course of investigations of the effect of antimony trichloride on promoting polymerization of α-olefins by Ziegler–Natta catalysts[1], it was found that antimony trichloride reacted with organoaluminum compounds in an unexpected manner to give organometallic complexes containing antimony and aluminum. Several authors had previously investigated the reactions of organoaluminum compounds with antimony trihalides[2-5]. However, the formation of such complexes has not been reported.

In order to study the above reactions and to prepare new complexes containing antimony and aluminum, a series of the reactions of alkylantimony compounds, *i.e.*, triethylantimony dihalide, tetraethylstibonium halides and triethylstibine, with various aluminum compounds, $AlEt_nCl_{3-n}$ (where n is 0, 1, 2 or 3), have been further investigated systematically.

RESULTS AND DISCUSSION

Reactions of antimony trichloride with aluminum alkyls

Antimony trichloride was found to react vigorously with an excess of triethylaluminum in n-hexane. The product separated into two layers and the lower layer contained a black powder which, after removal by filtration, proved to be metallic antimony. The lower layer, after repeated extraction with n-hexane and removal of antimony, but without further purification, gave analytical values in agreement with the formula $SbAl_2Et_9Cl_2$. Hydrolysis of this material with water evolved a gas which proved to consist of 95.8% ethane with trace of ethylene and hydrogen and 3.9% a C_4 hydrocarbon. The amount of ethane liberated was found to correspond to 52% of the ethyl groups present in the formula $SbAl_2Et_9Cl_2$. Since only ethyl groups bound to aluminum would be evolved as ethane on hydrolysis, this result suggests that the structure of the product is $[SbEt_4][Al_2Et_5Cl_2]$. The presence of tetraethylstibonium ion was demonstrated by its polarographic reduction and comparison with the reduction of a known tetraethylstibonium ion. The analytical value of the $SbEt_4^+$ content corresponded to 97% of the theoretical value for the above formula. The upper hexane layer from the original reaction was treated with water to hydrolyze the aluminum-containing products, and the hexane layer was separated and distilled. The principal product was identified by its infrared spectrum and analysis as triethylstibine. It thus appears that antimony trichloride reacts with triethylaluminum in n-hexane to produce approximately 46% $[SbEt_4][Al_2Et_5Cl_2]$, 42% metallic antimony and 10% triethylstibine or its complex which is soluble in n-hexane. The fact that 40 mole percent of the antimony trichloride was reduced to metallic antimony and the rest mostly oxidized to a complex of quinquevalent antimony indicates the following redox reaction:

$$5\,Sb(III) \rightarrow 3\,Sb(V) + 2\,Sb(0) \qquad (1)$$

Accordingly, the overall reaction can be written as follows:

$$SbCl_3 + AlEt_3\text{ (excess)} \rightarrow \tfrac{3}{5}\,[SbEt_4][Al_2Et_5Cl_2] + \tfrac{2}{5}\,Sb + AlEt_nCl_{3-n}\text{ (excess)} \qquad (2)$$

The formation of a small amount of triethylstibine or its complex might result from a side reaction. Judging from the fact that metallic antimony was formed quantitatively according to equation (1), some antimony(V) compound, which was once formed, might decompose to yield triethylstibine or its complex. It is noted that the reaction proceeds in a different way when a polar solvent is used. Zakharkin and Okhlobystin[3] reported that trialkylstibines were obtained in high yields by treating antimony trihalides with trialkylaluminums in ether.

The reaction of antimony trichloride with an excess of diethylaluminum chloride proceeded similarly, liberating metallic antimony and causing separation of the reaction mixture into two liquid layers. From the lower layer white crystals were isolated after repeated extraction with n-hexane; these gave analytical values in agreement with the formula $SbAlEt_4Cl_4$. Hydrolysis of this material evolved substantially no gas and yielded $SbEt_4^+$ quantitatively. These results suggest that the structure of the product is $[SbEt_4][AlCl_4]$. The overall reaction can be written as follows:

$$SbCl_3 + AlEt_2Cl\text{ (excess)} \rightarrow \tfrac{3}{5}\,[SbEt_4][AlCl_4] + \tfrac{2}{5}\,Sb + AlEt_nCl_{3-n}\text{ (excess)} \qquad (3)$$

The reaction may be considered to consist of the following three steps:
(*a*) alkylation of antimony(III) chloride with aluminum alkyls;
(*b*) redox reaction between antimony(III) compounds;
(*c*) complex formation between antimony(V) compounds and aluminum alkyls.
In the first step various alkylantimony(III) compounds, $SbEt_nCl_{3-n}$ ($n = 1$, 2 or 3), may be formed. The next step may be the reaction between various antimony(III) compounds, $SbEt_nCl_{3-n}$, including unreacted antimony trichloride. In conformity with previous results found for trimethylstibine[6], triethylstibine was found to react with antimony trichloride with the formation of triethylantimony dichloride and metallic antimony as follows:

$$2\,SbCl_3 + 3\,SbEt_3 \rightarrow 3\,SbEt_3Cl_2 + 2\,Sb \qquad (4)$$

The same or similar redox reactions can reasonably be expected to occur. The third step may be the complex formation of an alkylantimony(V) compound with alkylaluminum compounds. For example, the following reactions are expected to occur, giving the complexes mentioned above:

$$SbEt_3Cl_2+AlEtCl_2 \rightarrow [SbEt_4][AlCl_4] \quad (5)$$
$$SbEt_3Cl_2+2\,AlEt_3 \rightarrow [SbEt_4][Al_2Et_5Cl_2] \quad (6)$$

The complex formations of the alkylantimony compounds with the aluminum compounds will be discussed below in detail.

Reactions of triethylantimony dichloride with aluminum compounds, $AlEt_nCl_{3-n}$

Triethylantimony dichloride was found to react rapidly with the aluminum compounds, $AlEt_nCl_{3-n}$ ($n=3$, 2, 1 and 0), to give a series of complexes containing antimony and aluminum, which were insoluble in aliphatic hydrocarbons. The results are summarized in Table 1. The formulas of the complexes were postulated on the basis of the chemical analysis and determination of the active ethyl groups, which were evolved as ethane on hydrolysis.

All the reactions of triethylantimony dichloride with the aluminum compounds having at least one ethyl group yielded stibonium complex salts. It was confirmed that reactions (5) and (6) occurred quantitatively and gave the complexes identical in their infrared spectra, analyses and melting points with the complexes obtained by the reactions of antimony trichloride with triethylaluminum and with diethylaluminum chloride, respectively. This fact is thought to provide evidence for the mechanism proposed before. The other reactions can be shown by the following equations:

$$SbEt_3Cl_2+AlEt_3 \rightarrow [SbEt_4][AlEt_2Cl_2] \quad (7)$$
$$SbEt_3Cl_2+AlEt_2Cl \rightarrow [SbEt_4][AlEtCl_3] \quad (8)$$

Both reactions (7) and (8) proceeded quantitatively. The complex $[SbEt_4][AlEtCl_3]$ could exist unchanged even though a large excess of diethylaluminum chloride was present. When an excess of ethylaluminum dichloride was reacted with triethylantimony dichloride, the product was gelatinous solid, which, however, was nearly identical in its infrared spectra and chemical analysis with the equimolar reaction product, $[SbEt_4][AlCl_4]$. It seems that the complex $[SbEt_4][AlCl_4]$ can also exist almost unchanged in the presence of excess ethylaluminum dichloride, and some contaminant of unknown nature has made the product gelatinous.

The reaction of triethylantimony dichloride with aluminum chloride gave various products depending on the reactant ratios. The equimolar reaction product was a 1 : 1 complex represented as $SbEt_3Cl_2\cdot AlCl_3$. Gas evolution was not observed on hydrolysis. When this material was dissolved in water, an equimolar amount of triethylantimony dichloride was isolated. These results suggest that the complex is a simple adduct.

$$SbEt_3Cl_2+AlCl_3 \rightarrow SbEt_3Cl_2\cdot AlCl_3 \quad (9)$$

The liquid product obtained by the reaction of triethylantimony dichloride with excess aluminum chloride could not be isolated completely from the unreacted material. The infrared spectrum of this product showed two strong peaks at 9.5 and 12.65 μ. Since neither triethylantimony dichloride nor the complex $SbEt_3Cl_2\cdot AlCl_3$ showed peaks in this region, the existence of another product is suggested.

Reactions of tetraethylstibonium halide with aluminum compounds, $AlEt_nCl_{3-n}$

The reactions of tetraethylstibonium halides, *i.e.*, tetraethylstibonium chloride

TABLE 1

REACTIONS OF $SbEt_3Cl_2$ WITH $AlEt_nCl_{3-n}$

Reaction condition				*n-Hexane-insoluble product*								
$AlEt_nCl_{3-n}$ Formula	*g*	*$AlEt_nCl_{3-n}$/$SbEt_3Cl_2$ molar ratio*	*Reaction temp. (°C) × time (h)*	*g*	*Appearance*	*Analysis found (calcd.) (%)*						*Proposed formula*
						Sb	*Al*	*Cl*	*C*	*H*	*$(C_2H_5)_n$*[a]	
$AlEt_3$	5.7	1.0	20×2	17.9	Colorless liquid	31.16 (30.90)	6.61 (6.85)	19.09 (18.00)	35.59 (36.58)	7.57 (7.67)	14.7 (14.7)	$[SbEt_4][AlEt_2Cl_2]$
$AlEt_3$	14.4	2.4	20×2	23.2	Colorless liquid	24.23 (23.96)	10.29 (10.62)	14.25 (13.96)	42.32 (42.54)	8.72 (8.92)	27.5 (28.6)	$[SbEt_4][Al_2Et_5Cl_2]$
$AlEt_2Cl$	7.2	1.0	60×16	24.0	White crystals[b]	30.32 (30.41)	6.02 (6.74)	26.26 (26.57)	28.45 (29.97)	5.98 (6.29)	6.3 (7.3)	$[SbEt_4][AlEtCl_3]$
$AlEt_2Cl$	9.6	2.0	60×16	15.5	White crystals[b]	29.49 (30.41)	6.74 (6.74)	26.88 (26.57)	29.77 (29.97)	6.30 (6.29)	7.5 (7.3)	$[SbEt_4][AlEtCl_3]$
$AlEtCl_2$	4.6	1.0	20×20	14.5	White crystals	29.83 (29.93)	6.66 (6.63)	34.57 (34.87)	23.14 (23.62)	4.89 (4.95)	0 (0)	$[SbEt_4][AlCl_4]$
$AlEtCl_2$	9.1	2.0	20×20	15.5	Pale yellow gelatinous solid	29.25 (29.93)	6.97 (6.63)	37.12 (34.87)	22.02 (23.62)	4.66 (4.95)	0 (0)	$[SbEt_4][AlCl_4]$
$AlCl_3$	4.8	1.0	20×20	14.6	White crystals[c]	29.85 (29.47)	6.58 (6.53)	42.12 (42.91)	17.85 (17.44)	3.92 (3.66)	0 (0)	$SbEt_3Cl_2 \cdot AlCl_3$
$AlCl_3$	9.6	2.0	20×20	17.7[d]	Dark green liquid							$SbEt_3Cl_2 \cdot nAlCl_3$?

[a] $(C_2H_5)_n$ is the active ethyl group which was evolved as ethane on hydrolysis. [b] M.p. ca. 35°. [c] M.p. ca. 50°. [d] $AlCl_3$ (2.0 g) was recovered from the resulting mixture.

TABLE 2

REACTIONS OF Et_4SbCl WITH $AlEt_nCl_{3-n}$

Et_4SbCl: 73.3 mmoles (20.0 g), 50° × 1 h

Reactant			*n-Hexane insoluble product*								
$AlEt_nCl_{3-n}$		*$AlEt_nCl_{3-n}$/$SbEt_4Cl$ molar ratio*	*g*	*Appearance*	*Analysis found (calcd.) (%)*						*Proposed formula*
Formula	*g*				*Sb*	*Al*	*Cl*	*C*	*H*	*$(C_2H_5)_n$*[b]	
$AlEt_3$	8.35	1.0	27.2	Colorless liquid	32.22 (31.41)	6.68 (6.96)	9.83 (9.15)	42.95 (43.38)	9.35 (9.10)	19.4 (22.4)	$[SbEt_4][AlEt_3Cl]$
$AlEt_3$	25.1	3.0	32.7	Colorless liquid	24.58 (24.75)	10.68 (10.75)	8.01 (7.07)	47.76 (47.87)	10.00 (10.04)	33.9 (34.7)	$[SbEt_4][Al_2Et_6Cl]$
$AlEt_2Cl$	8.84	1.0	28.8	Colorless liquid	31.89 (30.90)	6.98 (6.85)	18.26 (18.00)	36.79 (36.58)	8.05 (7.67)	14.3 (14.7)	$[SbEt_4][AlEt_2Cl_2]$
$AlEt_2Cl$	26.5	3.0	35.3	Colorless liquid	25.59 (25.58)	9.51 (9.52)	20.36 (19.96)	37.26 (37.14)	7.81 (7.79)	21.0 (20.5)	$[SbEt_4][Al_2Et_4Cl_3]$ $+[SbEt_4][AlEt_2Cl_2]$
$AlEtCl_2$	9.30	1.0	28.7	White crystals	30.89 (30.46)	6.91 (6.75)	26.83 (26.62)	29.53 (30.00)	6.23 (6.25)	6.73 (7.25)	$[SbEt_4][AlEtCl_3]$
$AlEtCl_2$	27.9	3.0	29.0	White crystals	29.83 (29.95)	6.62 (6.64)	34.79 (34.90)	23.51 (23.60)	4.79 (4.91)	0 (0)	$[SbEt_4][AlCl_4]$
$AlCl_3$	9.77	1.0	29.6[a]	White crystals	30.23 (29.95)	6.87 (6.64)	34.42 (34.90)	23.31 (23.60)	5.03 (4.91)	0 (0)	$[SbEt_4][AlCl_4]$
$AlCl_3$	29.3	3.0	47.1[a]	Orangish brown liquid	18.09	11.60	45.63	19.40	3.88	0	$[SbEt_4][Al_nCl_{3n+1}]$?

[a] Benzene-insoluble product. [b] $(C_2H_5)_n$ is the active ethyl group which was evolved as ethane on hydrolysis. [c] Calculated assuming that 1.68 moles of $AlEt_2Cl$ was combined to $SbEt_4Cl$.

TABLE 3

REACTIONS OF Et_4SbI WITH $AlEt_nCl_{3-n}$

Et_4SbI: 35 mmoles (12.8 g), 70° × 15 h

Reactant			*n*-Hexane-insoluble product									
$AlEt_nCl_{3-n}$		$AlEt_nCl_{3-n}$/$SbEt_4I$ molar ratio	*g*	*Appearance*	*Analysis found (calcd.) (%)*							*Proposed formula*
Formula	*g*				*Sb*	*Al*	*Cl*	*I*	*C*	*H*	$(C_2H_5)_n$[b]	
$AlEt_3$	4.0	1.0	15.7	Colorless liquid	24.69 (25.42)	5.57 (5.64)	0 (0)	27.11 (26.49)	34.72 (35.10)	7.59 (7.36)	18.3 (18.19)	$[SbEt_4][AlEt_3I]$
$AlEt_3$	8.0	2.0	19.8	Colorless liquid	22.01 (22.05)	8.02 (8.01)	0 (0)	22.42 (22.98)	39.23 (38.81)	8.05 (8.14)	24.2 (25.90)	$[SbEt_4][Al_2Et_6I]$ $+[SbEt_4][AlEt_3I]$[c]
$AlEt_2Cl$	4.2	1.0	16.5	Colorless liquid	25.95 (25.08)	5.35 (5.56)	8.09 (7.30)	25.32 (26.16)	29.81 (29.69)	6.45 (6.23)	11.5 (11.97)	$[SbEt_4][AlEt_2ClI]$
$AlEt_2Cl$	8.4	2.0	19.1	Colorless liquid	20.97 (20.09)	9.21 (8.90)	10.93 (11.70)	21.02 (20.94)	31.54 (31.71)	6.29 (6.65)	17.3 (19.18)	$[SbEt_4][Al_2Et_4Cl_2I]$
$AlEtCl_2$	4.4	1.0	17.1	White crystals	23.86 (24.57)	5.81 (5.49)	14.64 (14.42)	25.13 (25.80)	24.96 (24.42)	5.01 (5.12)	5.8 (5.91)	$[SbEt_4][AlEtCl_2I]$
$AlEtCl_2$	8.8	2.0	16.9	White crystals	24.80 (24.44)	5.88 (5.41)	22.11 (21.35)	— (25.47)	19.49 (19.28)	4.20 (4.05)	0.9 (0)	$[SbEt_4][AlCl_3I]$
$AlCl_3$	4.7	1.0	17.4[a]	Brown crystals	24.86 (24.44)	5.71 (5.41)	21.96 (21.35)	— (25.47)	19.30 (19.28)	4.04 (4.05)	0 (0)	$[SbEt_4][AlCl_3I]$
$AlCl_3$	9.4	2.0	21.0[a]	Reddish orange liquid	19.35 (19.28)	8.57 (8.54)	33.53 (33.68)	— (20.09)	15.20 (15.21)	3.08 (3.19)	0 (0)	$[SbEt_4][Al_2Cl_6I]$?

[a] Benzene-insoluble product. [b] $(C_2H_5)_n$ is the active ethyl group which was evolved as ethane on hydrolysis. [c] Calculated assuming that 1.64 moles of $AlEt_3$ was combined to $SbEt_4I$.

and tetraethylstibonium iodide, with the aluminum compounds, $AlEt_nCl_{3-n}$ ($n = 3$, 2, 1 and 0), proceeded rapidly to give a series of stibonium complex salts, which were insoluble in hydrocarbons. The results of the reactions and the analysis of the products are summarized in Tables 2 and 3.

The reactions can be written by the following equations:

$$SbEt_4X + AlEt_3 \rightarrow [SbEt_4][AlEt_3X] \tag{10}$$
$$SbEt_4X + 2\,AlEt_3 \rightarrow [SbEt_4][Al_2Et_6X] \tag{11}$$
$$SbEt_4X + AlEt_2Cl \rightarrow [SbEt_4][AlEt_2XCl] \tag{12}$$
$$SbEt_4X + 2\,AlEt_2Cl \rightarrow [SbEt_4][Al_2Et_4XCl_2] \tag{13}$$
$$SbEt_4X + AlEtCl_2 \rightarrow [SbEt_4][AlEtXCl_2] \tag{14}$$
$$SbEt_4X + 2\,AlEtCl_2 \rightarrow [SbEt_4][AlXCl_3] + AlEt_2Cl \tag{15}$$
$$SbEt_4X + AlCl_3 \rightarrow [SbEt_4][AlXCl_3] \tag{16}$$

where X is halogen. Reactions (11) and (13) in which tetraethylstibonium iodide and tetraethylstibonium chloride were used respectively did not proceed quantitatively and gave mixtures of the 1:1 and 1:2 complexes. All the other reactions were quantitative. In reaction (15), the 1:1 complex $[SbEt_4][AlEtXCl_2]$ resulting from reaction (14) may further react with excess ethylaluminum dichloride as follows:

$$[SbEt_4][AlEtXCl_2] + AlEtCl_2 \rightarrow [SbEt_4][AlXCl_3] + AlEt_2Cl \tag{17}$$

It is noted that the complex $[SbEt_4][AlXCl_3]$ and diethylaluminum chloride can coexist under ordinary conditions, and the iodine atom is bound to aluminum predominantly in the aluminate ion.

When excess aluminum chloride was reacted, the unreacted aluminum chloride could not be removed from the product. The infrared spectrum of the product showed a strong peak at about 12.7 μ. Since the 1:1 complex, $[SbEt_4]\cdot[AlXCl_3]$, showed no peak in this region, the presence of another material is suggested.

Ionic properties of the complexes

The stibonium complex salts obtained by the reactions before mentioned can be represented by the following general formulas:

$$[SbEt_4][AlEt_nX_{4-n}] \quad (1:1 \text{ complex}) \tag{I}$$
$$[SbEt_4][Al_2Et_nX_{7-n}] \quad (1:2 \text{ complex}) \tag{II}$$

These complexes have remarkable ionic properties. Table 4 shows electrical conductivities of some of these complexes. This result suggests the ionic structures of the com-

TABLE 4

ELECTRICAL CONDUCTIVITIES OF THE COMPLEXES

Complex	*Specific conductance ($\mho$/cm)*
$[SbEt_4][AlEt_3Cl]$	3.44×10^{-3} (25°)
$[SbEt_4][AlEt_3I]$	2.64×10^{-3} (25°)
$[SbEt_4][AlEt_2Cl_2]$	3.94×10^{-3} (25°)
$[SbEt_4][AlEtCl_3]$	3.10×10^{-3} (50°)
$[SbEt_4][Al_2Et_6Cl]$	3.64×10^{-3} (25°)

plexes as shown by ionic formulas as $[SbEt_4]^+[AlEt_nX_{4-n}]^-$ and $[SbEt_4]^+\cdot[Al_2Et_nX_{7-n}]^-$, respectively.

Reactions of 1 : 1 *complexes,* $[SbEt_4][AlEt_nCl_{4-n}]$, *with aluminum alkyls*

A series of the reactions between the 1 : 1 complexes and aluminum compounds, $AlEt_nCl_{3-m}$, were found to proceed as follows:

$$[SbEt_4][AlEt_3Cl] + AlEt_3 \rightarrow [SbEt_4][Al_2Et_6Cl] \tag{18}$$

$$[SbEt_4][AlEt_3Cl] + AlEt_2Cl \rightarrow [SbEt_4][Al_2Et_5Cl_2] \tag{19}$$

$$[SbEt_4][AlEt_3Cl] + AlEtCl_2 \rightarrow \text{mixed complex?} \tag{20}$$

$$[SbEt_4][AlEt_2Cl_2] + AlEt_3 \rightarrow [SbEt_4][Al_2Et_5Cl_2] \tag{21}$$

$$[SbEt_4][AlEt_2Cl_2] + AlEt_2Cl \rightarrow [SbEt_4][Al_2Et_4Cl_3] \tag{22}$$

$$[SbEt_4][AlEt_2Cl_2] + 2\,AlEtCl_2 \rightarrow [SbEt_4][AlCl_4] + 2\,AlEt_2Cl \tag{23}$$

$$[SbEt_4][AlEtCl_3] + AlEt_3\ (\text{excess}) \rightarrow [SbEt_4][Al_2Et_5Cl_2] \tag{24}$$

$$[SbEt_4][AlEtCl_3] + AlEt_2Cl \rightarrow \text{unchanged} \tag{25}$$

$$[SbEt_4][AlEtCl_3] + AlEtCl_2 \rightarrow [SbEt_4][AlCl_4] + AlEt_2Cl \tag{26}$$

$$[SbEt_4][AlCl_4] + AlEt_3\ (\text{excess}) \rightarrow [SbEt_4][Al_2Et_5Cl_2] \tag{27}$$

$$[SbEt_4][AlCl_4] + AlEt_2Cl \rightarrow \text{unchanged} \tag{28}$$

These reactions involve several types of reactions, *e.g.*, (*a*) ethylation of the aluminate ion [(24) and (27)], (*b*) chlorination of the aluminate ion [(23) and (26)], (*c*) formation of the 1 : 2 complexes [(18), (19), (21) and (22)] and (*d*) ligand exchange reaction of the 1 : 2 complexes as shown below:

$$[SbEt_4][Al_2Et_nCl_{7-n}] + AlEt_mCl_{3-m} \rightarrow [SbEt_4][Al_2Et_{n'}Cl_{7-n'}] + AlEt_{m'}Cl_{3-m'} \tag{29}$$

In reactions (24) and (27), various complexes were obtained depending on the reactant ratios. When $[SbEt_4][AlEtCl_3]$ was reacted with 2 moles of triethylaluminum, the product was analysed to be $[SbEt_4][(AlEt_2Cl)_{1.33}(AlEt_3)_{0.56}Cl]$. As illustrated in Fig. 1, when $[SbEt_4][AlCl_4]$ was reacted with a large excess of triethylaluminum, the product was identified as $[SbEt_4][Al_2Et_5Cl_2]$. Consequently, the above complex $[SbEt_4][(AlEt_2Cl)_{1.33}(AlEt_3)_{0.56}Cl]$ may further react with triethylaluminum to yield $[SbEt_4][Al_2Et_5Cl_2]$ according to equation (29).

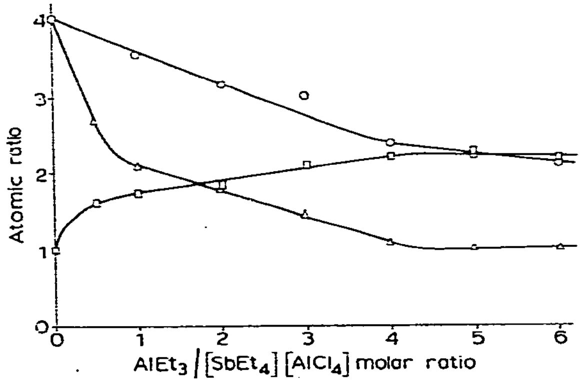

Fig. 1. Composition of the n-hexane insoluble products obtained by the reaction of $[SbEt_4][AlCl_4]$ with triethylaluminum: □, Al/Sb; △, Cl/Al; ○, Cl/Sb.

Reactions of triethylstibine with aluminum compounds, $AlEt_nCl_{3-n}$

Triethylstibine was found to react rapidly with triethylaluminum, diethyl-

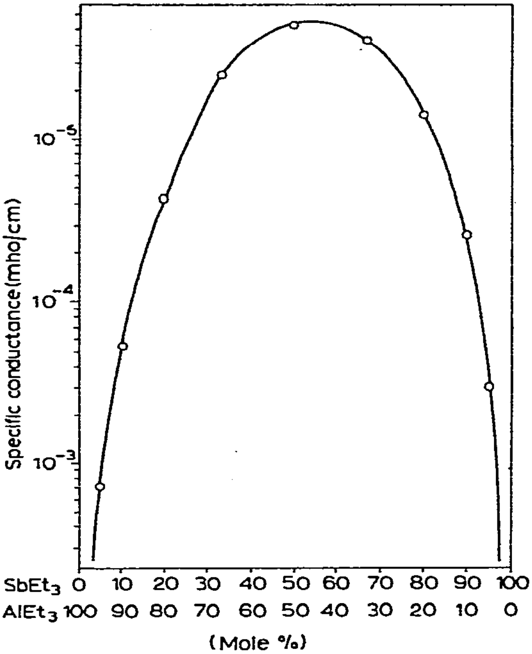

Fig. 2. Electrical conductivity of the mixture of $AlEt_3$ and $SbEt_3$.

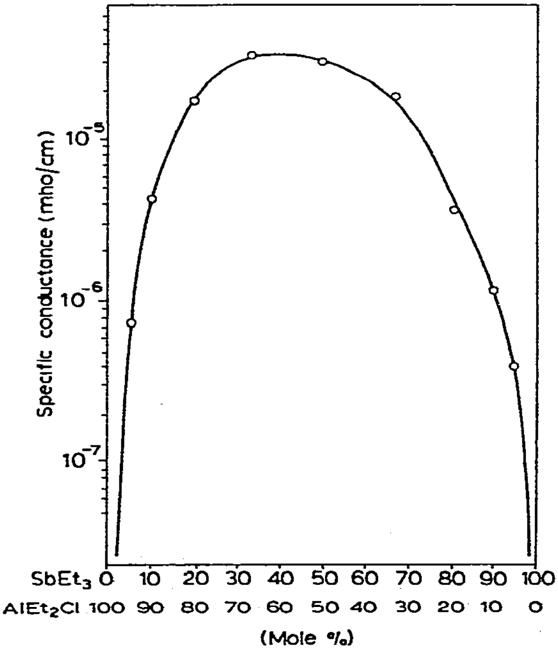

Fig. 3. Electrical conductivity of the mixture of $AlEt_2Cl$ and $SbEt_3$.

aluminum chloride and ethylaluminum dichloride at room temperature to give products which were soluble in aliphatic hydrocarbons. The coordination compounds $m\mathrm{SbEt_3}\cdot n\mathrm{AlEt}_{n'}\mathrm{Cl}_{3-n'}$, not yet identified, are postulated to have been formed as in the cases of tertiary amines, ethers, and tertiary phosphines[7]. The reaction mixtures showed remarkably high electrical conductivities as shown in Figs. 2, 3 and 4. This result suggestst that these complexes have ionic structures.

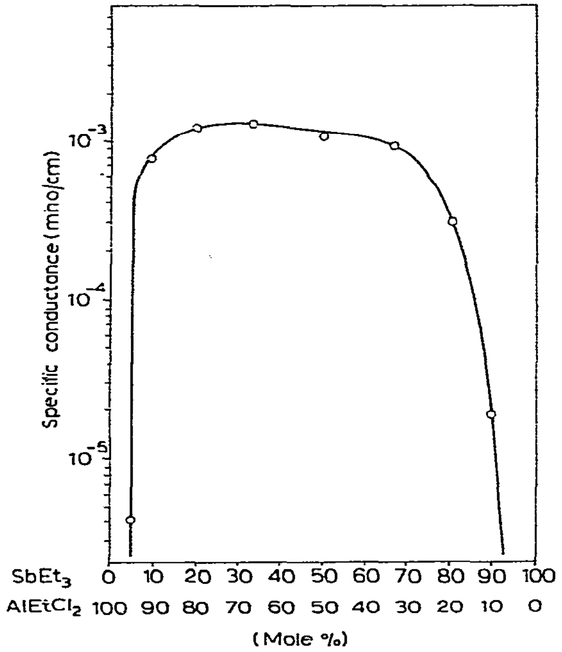

Fig. 4. Electrical conductivity of the mixture of $\mathrm{AlEtCl_2}$ and $\mathrm{SbEt_3}$.

The reaction of triethylstibine with aluminum chloride proceeded at 60° to give 2 types of complexes insoluble in n-hexane, depending on the reactant ratios. The equimolar reaction gave a yellowish green liquid quantitatively, which gave analytical values in agreement with the formula $\mathrm{SbEt_3\cdot AlCl_3}$. (Found: C, 20.65; H, 4.25; Al, 7.13; Cl, 31.06; Sb, 36.91. Calcd.: C, 21.05; H, 4.41; Al, 7.88; Cl, 31.08; Sb, 35.58%.) By reacting a large excess of triethylstibine with 4.0 g of aluminum chloride, 8.6 g of yellowish brown crystals were obtained, and the analytical values of this material agreed with the calculated values for the 2:1 adduct $\mathrm{SbEt_3\cdot SbEt_2Cl\cdot AlCl_3}$. (Found: C, 21.33; H, 4.47; Al, 4.56; Cl, 26.32; Sb, 42.86. Calcd.: C, 21.52; H, 4.52; Al, 4.84; Cl, 25.44; Sb, 43.67%.) This result suggests that the 1:1 adduct $\mathrm{SbEt_3\cdot AlCl_3}$ reacts with excess triethylstibine to give the 2:1 adduct $\mathrm{SbEt_3\cdot SbEt_2Cl\cdot AlCl_3}$, and that in this reaction an alkylation of aluminum chloride ligand with triethylstibine occurs. The product soluble in n-hexane contained an appreciable amount of active ethyl groups, suggesting the presence of an ethylaluminum compound, which might have resulted from the alkylation as postulated above.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of dry and oxygen-free nitrogen. Electrical conductivities were measured by a Toa–Dempa Electric Conductometer fitted with platinum-black poles.

Materials

A commercial reagent of antimony trichloride was purified by distillation *in vacuo*. Triethylstibine[8,9], triethylantimony dichloride, tetraethylstibonium iodide[10] were prepared by known procedures. Tetraethylstibonium chloride was prepared by the metathetical reaction between tetraethylstibonium iodide and cuprous chloride in aqueous or in alcoholic solution. (In keeping with the work of previous authors[10], we have found that triethylstibine is quaternized so slowly when ethyl chloride is used as the quaternizing agent as to render the reaction useless for synthetic purposes.) Aluminum alkyls supplied from Texas Alkyl Corp. were used without further purification. Aluminum chloride was a commercial reagent (Kishida Chem. Co., special reagent grade). All solvents were refluxed over sodium wire, distilled and stored over a molecular sieve.

Analysis

Determination of active alkyl groups and hydride. These groups were determined by measuring the amount of gas liberated on hydrolysis. Hydrolysis was carried out by treating the sample with moisture at room temperature.

Determination of tetraethylstibonium ion. Tetraethylstibonium ion was analysed by the polarographic method. A sample was dissolved in a large quantity of benzene and hydrolyzed by the addition of water. After stripping the benzene, the aqueous solution was analysed by conventional method, using a Yanagimoto PA-2 type polarograph. Potassium chloride (1 mole/l) and gelatine (0.01%) were used as the supporting electrolyte and the maximum suppressor, respectively. The pH of the solution was adjusted at 7–10 using sodium bicarbonate. Tetraethylstibonium ion showed two plateau waves in the range of -1.0 to -2.0 volts. The half wave potentials were around -1.3 and -1.7 volts.

Reaction of antimony trichloride with triethylaluminum

Into a 2 l flask equipped with a mercury sealed stirrer, an addition funnel and a reflux condenser were placed 0.878 mole of antimony trichloride and 150 ml of n-hexane. Triethylaluminum (5.27 moles) was added dropwise with stirring under reflux. A vigorous reaction took place, liberating a black solid. After the addition, stirring was continued for an additional 30 min. The reaction mixture consisted of a black powder and two colorless liquid layers. The lower liquid layer containing the black powder was syphoned and filtered from the black powder. The filtrate was washed repeatedly with n-hexane and then evaporated at 70°/2 mm. The black powder was washed with benzene. The benzene washings were evaporated, and extracted with n-hexane, leaving an isoluble liquid. The average yields of the liquid product insoluble in n-hexane and the black powder were 203 g and 45 g respectively for three runs. The liquid product insoluble in n-hexane was analyzed. (Found: C, 43.05;

H, 8.97; Al, 10.58; Cl 13.28; Sb, 24.14. $C_{18}H_{45}AlCl_2Sb$ calcd.: C, 42.54; H, 8.92; Al, 10.62; Cl, 13.96; Sb, 23.96%.) The black powder was analyzed as pure antimony.

The product soluble in n-hexane was isolated as follows. Antimony trichloride (1.27 moles, 290 g) was treated with 7 moles of triethylaluminum (798 g) in 150 ml of n-hexane, according to the method mentioned above. The product was extracted with n-hexane, and 1,250 g of n-hexane solution was obtained. To 195 g of the solution in a similar flask was added dropwise 600 ml of water with stirring. The n-hexane phase was evaporated, leaving 13.7 g of pale yellow liquid. The product was distilled under reduced pressure, and the principal fraction (4.3 g, b.p. 53°/15 mm) was identified by its IR spectrum and chemical analysis as impure triethylstibine. (Found: C, 34.20; H, 8.16; Cl, 0.00; Sb, 56.77. $C_6H_{15}Sb$ calcd.: C, 34.40; H, 7.24; Sb, 58.28%.)

Reaction of antimony trichloride with diethylaluminum chloride

In a manner similar to the above experiment, 3.72 moles of diethylaluminum chloride was added dropwise to a mixture of 0.62 mole of antimony trichloride and 200 ml of n-hexane under reflux over a 2 h period. The mixture was stirred under reflux for an additional 30 min. The reaction mixture consisted of a black solid and two colorless liquid layers. After removal of the black solid by filtration, the lower layer was extracted repeatedly with a large amount of n-hexane. White crystals separated during the extraction, and were dried *in vacuo*. The yield was 81 g., m.p. 185°. (Found: C, 23.47; H, 5.26; Al, 6.40; Cl, 34.39; Sb, 28.8. $C_8H_{20}AlCl_4Sb$ calcd.: C, 23.62; H, 4.95; Al, 6.63; Cl, 34.87; Sb, 29.93%.)

Reaction between antimony trichloride and triethylstibine

Antimony trichloride (18.2 g, 0.080 mole) and 50 ml of n-hexane were placed into a 100 ml flask equipped with a reflux condenser, a dropping funnel and a magnetic stirrer. Triethylstibine (25.2 g, 0.12 mole) was added dropwise at 70° with stirring. The reaction proceeded vigorously, liberating a precipitate. The reaction mixture was refluxed for an additional 10 minutes, and left overnight at room temperature. The precipitate was filtered, washed with benzene and dried under reduced pressure, leaving 10.0 g of a black powder which was proved to be metallic antimony (0.080 mole). The filtrate, after removal of the solvent, gave 30.9 g of a pale yellow liquid. The liquid product (22.5 g) was fractionated under reduced pressure. The principal fraction (19.3 g, b.p. 123.5°/3 mm) was identified by its IR spectrum and chemical analysis as triethylantimony dichloride. (Found: C, 26.16; H, 5.80; Cl, 25.47; Sb, 43.74. $C_6H_{15}Cl_{12}Sb$ calcd.: C, 25.75; H, 5.40; Cl, 25.34; Sb, 43.50%.) Yield, 0.095 mole.

Reactions of triethylantimony dichloride with aluminum compounds

Two reagents were mixed at room temperature, and shaken in a sealed ampoule. The experimental conditions are given in Table 1. The reaction mixture was extracted with dry n-hexane repeatedly, and the products insoluble in n-hexane were isolated. In the reaction of aluminum chloride, unreacted aluminum chloride was filtered off, the solvent (benzene) was removed from the product, and then the remaining product was treated with n-hexane as described above.

Reactions of tetraethylstibonium halides with aluminum compounds

Tetraethylstibonium chloride. The experimental conditions are given in Table 2. To a suspension of tetraethylstibonium chloride in 20 ml of n-hexane was added a quantity of ethylaluminum compound dropwise at −10° with stirring. After the addition, the reaction mixture was stirred at 50° for 1 h, and treated with n-hexane by the usual procedure as described before.

Powdered aluminum trichloride was added to the solution of tetraethylstibonium chloride in 50 ml of benzene at room temperature over a 15 min period. The reaction was carried out in a similar manner, and the reaction mixture was extracted with benzene, leaving an insoluble product.

Tetraethylstibonium iodide. Two reagents were mixed at room temperature (Table 3). The reaction mixture was shaken in a sealed ampoule at 70° for 15 h. Benzene (50 ml) was used as the solvent for the reaction with aluminum chloride. The products were treated as described in the above experiment.

Reactions of the 1:1 complexes $[SbEt_4][AlEt_nX_{4-n}]$ with aluminum compounds

Reaction of $[SbEt_4][AlEt_3Cl]$ with diethylaluminum chloride. Into a 50 ml glass ampoule equipped with an addition funnel and a magnetic stirrer were placed 0.0366 mole (10.00 g) of tetraethylstibonium chloride and 20 ml of n-hexane. An equimolar amount of triethylaluminum (4.20 g) dissolved in 5 ml of n-hexane was added dropwise at −50° with stirring. After the addition, the reaction mixture was warmed at 50° for 1 h to complete the formation of the 1:1 complex, $[SbEt_4]\cdot[AlEt_3Cl]$. To this mixture was added dropwise an equimolar quantity of diethylaluminum chloride (4.48 g) at room temperature. The ampoule was sealed and shaken at 60° for 24 h. The resulting mixture was filtered from a trace of black solid, and the filtrate was washed with n-hexane repeatedly, and evaporated under reduced pressure, leaving 16.20 g of a liquid product. The content of active ethyl groups was 26.3%; calcd. for $[SbEt_4][Al_2Et_5Cl_2]$: 28.6%. The IR spectrum coincided with that of the complex $[SbEt_4][Al_2Et_5Cl_2]$ obtained by the other methods as described before.

Reaction of $[SbEt_4][AlEt_2Cl_2]$ with triethylaluminum. To 0.0366 mole of tetraethylstibonium chloride (10.00 g) was added an equimolar quantity of diethylaluminum chloride (4.43 g) and triethylaluminum (4.20 g) successively, according to the procedure described in the above experiment. A liquid product (17.53 g) insoluble in n-hexane was obtained. The content of active ethyl groups was 29.5%; calcd. for $[SbEt_4][Al_2Et_5Cl_2]$: 28.6%. The IR spectrum coincided exactly within the wavelength range 3–25 μ with that of the product from $[SbEt_4][AlEt_3Cl]$ and diethylaluminum chloride.

Reaction of $[SbEt_4][AlEt_2Cl_2]$ with ethylaluminum dichloride. $[SbEt_4]\cdot[AlEt_2Cl_2]$ was prepared by the equimolar reaction of tetraethylstibonium chloride and diethylaluminum chloride in n-hexane. To 9.09 mmoles (3.58 g) of $[SbEt_4]\cdot[AlEt_2Cl_2]$ in a glass ampoule was added a large excess of ethylaluminum dichloride (55.7 mmoles, 7.07 g) at −30°. The ampoule was sealed and shaken at 80° for 33 h. The reaction mixture was treated with n-hexane as usual. There remained 3.80 g of pale yellow crystals. (Found: C, 21.98; H, 4.71; Al, 8.06; Cl, 37.30; Sb, 27.73; Et_a, 0.08. $[SbEt_4][AlCl_4]$ calcd.: C, 23.62; H, 4.95; Al, 6.63; Cl, 34.75; Sb, 29.95; Et_a, 0%.) The IR spectrum coincided with that of the complex $[SbEt_4][AlCl_4]$ obtained by the other methods described before.

Reaction of $[SbEt_4][AlEtCl_3]$ *with triethylaluminum.* $[SbEt_4][AlEtCl_3]$ was prepared by the equimolar reaction of tetraethylstibonium chloride with ethylaluminum dichloride. Triethylaluminum (0.0736 mole, 8.40 g) dissolved in 40 ml of n-hexane was added to 0.0368 mole (14.74 g) of $[SbEt_4][AlEtCl_3]$ with stirring at room temperature over a 30 min period. The reaction mixture was kept at 50° for 1 h. After having stood overnight the mixture was treated with n-hexane as usual, and 18.50 g of a liquid product insoluble in n-hexane was obtained. (Found: C, 40.72; H, 8.19; Al, 10.24; Cl, 16.61; Sb, 24.50; Et_a, 24.7. $[SbEt_4][(AlEt_2Cl)_{1.33}(AlEt_3)_{0.56}Cl]$ calcd.: C, 40.25; H, 8.44; Al, 10.24; Cl, 16.60; Sb, 24.46; Et_a, 25.4%.)

Reaction of $[SbEt_4][AlEtCl_3]$ *with diethylaluminum chloride.* Similarly, a mixture of 0.0382 mole (15.29 g) of $[SbEt_4][AlEtCl_3]$, 0.382 mole (4.61 g) of diethylaluminum chloride and 20 ml of *n*-hexane was stirred at 40–50° for 1.5 h. The starting complex was recovered quantitatively (15.27 g) by the usual treatment.

Reaction of $[SbEt_4][AlEtCl_3]$ *with ethylaluminum dichloride.* To an aliquot of $[SbEt_4][AlEtCl_3]$ which was molten at a temperature a little higher than its melting point (about 35°) was added ethylaluminum dichloride. The reaction mixture was shaken in a sealed ampoule at 70° for 17 h. When equimolar quantities of the two reagents were used, white crystals were obtained as the n-hexane-insoluble product (m.p. 187°). When an excess of ethylaluminum dichloride was used, the reaction mixture was a pale yellow, transparent liquid. After the repeated extraction with n-hexane, it gave fine crystals of slightly yellow color. The analytical data for each product nearly agreed with the formula $[SbEt_4][AlCl_4]$. The IR spectrum was also identical to that of the complex $[SbEt_4][AlCl_4]$ prepared before.

Reaction of $[SbEt_4][AlCl_4]$ *with triethylaluminum.* The reaction was carried out in a sealed ampoule at 70° for 17 h according to the usual manner. The product insoluble in n-hexane was isolated as usual. When a sufficiently large excess of triethylaluminum was reacted, the complex $[SbEt_4][Al_2Et_5Cl_2]$ was obtained quantitavely. (Found: C, 42.98; H, 9.00; Al, 11.04; Cl, 13.96; Sb, 22.93; Et_a, 29.0. $C_{18}H_{45}$-Al_2Cl_2Sb calcd.: C, 42.54; H, 8.92; Al, 10.62; Cl, 13.96; Sb, 23.96; Et_a, 28.6%.)

Reactions of triethylstibine with aluminum compounds

Triethylaluminum and diethylaluminum chloride. On mixing two reagents at room temperature, an exothermic reaction took place instantaneously. The mixture was left overnight, and then used for the conductometric measurements.

Ethylaluminum dichloride. Triethylstibine (3.0 g) and ethylaluminum dichloride were mixed in a wide range of molar ratios at −50°. After having been warmed gradually to 70°, the reaction mixture was left overnight at room temperature. By adding n-hexane, the reaction mixture was separated into two liquid layers. Extraction of the product with n-hexane was repeated several times at room temperature, leaving about 1 g of a residue. However, the residue was soluble in *n*-hexane to a certain extent and the extraction could not be accomplished completely.

Aluminum chloride. The reaction was carried out in a sealed ampoule at 60° for 20 h. The unreacted aluminum chloride was filtered off. The filtrate was treated with n-hexane as usual.

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SUMMARY

The reactions of antimony trichloride with excess triethylaluminum and with diethylaluminum chloride have been studied. The former reaction gives the complex $[SbEt_4][Al_2Et_5Cl_2]$ and the latter the complex $[SbEt_4][AlCl_4]$.

A series of the organometallic complexes containing antimony and aluminum has been prepared by the reactions of quinquevalent ethylantimony halides, *i.e.*, triethylantimony dihalide, tetraethylstibonium halides with various aluminum compounds, $AlEt_nCl_{3-n}$. The proposed formulas of these complexes are shown as $[SbEt_4][AlEt_nX_{4-n}]$ (I), $[SbEt_4][Al_2Et_nX_{7-n}]$ (II) and $SbEt_3X_2 \cdot nAlX_3$ (III), where X is halogen. The former two are thought to be ionic stibonium complex salts and the latter simple adducts. The behavior of 1:1 complex (I) for aluminum alkyls has further been clarified.

Triethylstibine also forms various complexes with aluminum compounds, $AlEt_nCl_{3-n}$. The proposed formulas of these complexes are shown as $mSbEt_3 \cdot nAlEt_{n'}Cl_{3-n'}$ (IV) and $SbEt_3 \cdot SbEt_2Cl \cdot AlCl_3$ (V). The ionic properties of complexes (IV) have been elucidated.

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