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Reactions of Alkylantimony Compounds with Titanium Chlorides

Yûkichi TAKASHI*[1]

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka

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The reactions of various alkylantimony compounds with titanium chlorides have been investigated. Tetraethylstibonium chloride was found to react with titanium tetrachloride to give the complex salts $[SbEt_4]_2TiCl_6$ (I), $[SbEt_4]TiCl_5$ (II) and $[SbEt_4]Ti_2Cl_9$ (III), and with titanium trichloride to give the complex salts $[SbEt_4]_2TiCl_5$ (VI) and $[SbEt_4]TiCl_4$ (V). Titanium dichloride was oxidized by tetraethylstibonium chloride to form the complex salts of tervalent titanium, IV and V. Triethylantimony dichloride made addition with titanium tetrachloride and afforded two or more ionic complexes, $SbEt_3Cl_2 \cdot TiCl_4$ and $(SbEt_3Cl_2)_m(TiCl_4)_n$. Titanium dichloride was oxidized by triethylantimony dichloride to give a complex of tervalent titanium, $SbEt_3 \cdot nTiCl_3$. Triethylstibine reduced titanium tetrachloride and formed an adduct of tervalent titanium, $SbEt_3Cl_2 \cdot 2TiCl_3$, when an excess of titanium tetrachloride was allowed to react. An excess of triethylstibine gave rise to complicated reactions with titanium tetrachloride, and formed $TiCl_3 \cdot mSbEt_3Cl_2 \cdot nSbt_3$ complexes.

Alkylantimony compounds have characteristic effects on the Ziegler-Natta catalyst in the polymerization of α-olefins; they promote the polymerization rate and improve the stereospecificity

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[1] Present address: Asahi Chemical Industry Co., Ltd., Nobeoka, Miyazaki.

of the catalyst.[1-4] In order to clarify the above catalytic reaction, studies of the reactions between the catalyst components are important. The reactions between alkylantimony compounds and alkylaluminum compounds have been studied systematically, and the rapid formation of various organometallic complexes containing antimony and aluminum has been demonstrated.[5] However, no study of the reaction between alkylantimony compounds and titanium chlorides has been reported.

In the present paper, the reactions of alkylantimony compounds, namely, tetraethylstibonium chloride, triethylantimony dichloride and triethylstibine, with titanium chlorides will be studied, and various novel complexes containing antimony and titanium will be described.

Experimental and Results

Materials. *Triethylstibine.* A commercial reagent (Sankyo Yûki Co.) was distilled at 60°C/50 mmHg.

Triethylantimony Dichloride. This reagent was prepared by the reaction of triethylstibine with chlorine according to the known procedure; bp 121°C/2 mmHg.

Tetraethylstibonium Chloride. The following reactions were used for its preparation:[5]

$$\mathrm{SbEt_3 + EtI \longrightarrow Et_4SbI} \tag{1}$$

$$\mathrm{Et_4SbI + CuCl \xrightarrow{MeOH} Et_4SbCl + CuI} \tag{2}$$

It was then recrystallized several times from tetrahydrofuran; mp 129—130°C.

Titanium Tetrachloride. A commercial reagent (Kishida Chem. Co.) was distilled at 136.0—136.4°C over metallic copper.

Titanium Trichloride. A commercial reagent (Stauffer Chem. Corp., HR Grade, α type) was used after evacuation at room temperature.

Titanium Dichloride. A commercial reagent (Tôhô Titanium Co.) was used after evacuation at room temperature.

Hydrocarbons. n-Hexane and benzene were purified according to ordinary methods. Petroleum ether was purified similarly, and a low boiling fraction (below 40°C) was used.

Analysis. The tetraethylstibonium ion was determined by the polarographic method.[5] Tetraethylstibonium chloride was isolated from the hydrolyzate as follows: An apropriate amount of the sample was hydrolyzed at room temperature. Titanium hydroxide was then precipitated by adding an aqueous solution of caustic soda and filtered off. The filtrate was neutralized with an aqueous hydrochloric acid solution. After the removal of water, tetraethylstibonium chloride was extracted from the residue with hot benzene. Triethylstibine and triethylantimony dichloride were isolated from the hydrolyzate by extraction with light petroleum ether under a purified nitrogen atmosphere in a closed glass apparatus. X-Ray powder diffractometric determination was carried out under a nitrogen atmosphere with a Shimadzu diffractometer GX-1 by the use of a scintillation counter and Cu$K\alpha$ radiation. For IR measurements a Hitatch Spectrophotometer EPI-2 was used. All the spectra of solid samples were taken by the Nujol method. The NMR spectrum was measured at room temperature in a benzene solution, using a Varian A-60 spectrometer operating at 60 Mc. For the measurement of the electrical conductivity, a Toa-Dempa Conductometer, Model CM-1D, equipped with platinium black poles was used.

Reactions of Tetraethylstibonium Chloride with Titanium Chlorides. *Titanium Tetrachloride.* To a benzene solution of tetraethylstibonium chloride in a glass ampoule, an aliquot of titanium tetrachloride was added drop by drop at room temperature under an oxygen-free, dry nitrogen atmosphere. The ampoule was then sealed and shaken at 30°C for 24 hr. Both the unreacted tetraethylstibonium chloride and the titanium tetrachloride were removed by extraction with benzene

TABLE 1. REACTION OF TETRAETHYL STIBONIUM CHLORIDE WITH TITANIUM TETRACHLORIDE

Temperature: 30°C, Time: 24 hr, Benzene: 200 cc

Reactants		Yield g (Theor.)	Appearence	n-Hexane-insoluble product Aanlysis[*1]						Postulated formula
$\mathrm{SbEt_4Cl}$ g	$\mathrm{SbEt_4Cl/TiCl_4}$ molel ratio			Sb%	Ti%	Cl%	C%	H%	$\mathrm{SbEt_4}^+$ %[*2]	
24.05	2.20	29.0[*3] (29.5)	Yellow Powder	33.56 (33.06)	6.19 (6.50)	28.38 (28.88)	25.99 (26.08)	5.38 (5.47)	61.82 (64.62)	$\mathrm{[SbEt_4]_2TiCl_6}$
18.23	1.00	30.0 (30.9)	Yellow Powder	26.06 (26.29)	10.21 (10.34)	37.70 (38.28)	20.64 (20.74)	4.25 (4.35)	48.33 (51.38)	$\mathrm{[SbEt_4]TiCl_5}$
13.67	0.45	31.5 (32.6)	Yellow Powder	19.02 (18.56)	13.80 (14.67)	47.93 (48.88)	14.98 (14.71)	3.07 (3.09)	35.43 (36.45)	$\mathrm{[SbEt_4]Ti_2Cl_9}$

[*1] Values in parentheses are calculated for the postulated formulas.

[*2] Amounts of tetraethylstibonium ion detected in the hydrolyzates.

[*3] Benzene-insoluble product.

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[1] Y. Takashi, I. Aishima, Y. Kobayashi and Y. Tsunoda (to Asahi Chemical Ind., Co.), Japanese Pat. 38-9441 (June 17, 1963).

[2] Y. Takashi, I. Aishima, Y. Kobayashi and Y. Tsunoda (to Asahi Chemical Ind., Co.), Japanese Pat. 40—17663 (Aug. 11, 1965).

[3] Y. Takashi and I. Aishima, to be published.

[4] H. W. Coover, Jr. (to Eastman Kodak Co.), Japanese Pat. 36-22440 (Dec. 20, 1961).

[5] Y. Takashi and I. Aishiama, to be published.

and *n*-hexane respectively. The results of the reaction are summarized in Table 1.

The IR spectra of the complexes closely resembled that of tetraethylstibonium chloride, suggesting the presence of the tetraethylstibonium ion structure. As is shown in Table 2, some shifts of the absorptions, which might be due to the difference in the ligands, were observed.

The powder X-ray diffraction patterns of the complexes are shown in Fig. 1. (The scales of *s* to *w* indicate the visually-estimated intensities.) The $[SbEt_4]_2TiCl_6$ and $[SbEt_4]TiCl_5$ complexes were highly crystalline, while $[SbEt_4]_2Ti_2Cl_9$ was amorphous.

All the complexes dissolved in either water or alcohols. They decomposed just below their melting points as follows: $[SbEt_4]_2TiCl_6$, 220—225°C (decomposed); $[SbEt_4]TiCl_5$, 147—152°C (decomposed); $[SbEt_4]Ti_2Cl_9$, 91—102°C (decomposed).

TABLE 2. MAIN INFRARED ABSORPTION SHIFTS OF THE STIBONIUM COMPLEX SALTS OF TITANIUM (IV AND III) AND STIBONIUM CHLORIDE(CM^{-1})

$SbEt_4Cl$	Ti(IV) complexes			Ti(III) complexes	
	$[SbEt_4]_2$ $TiCl_6$	$[SbEt_4]$ $TiCl_5$	$[SbEt_4]$ Ti_2Cl_9	$[SbEt_4]_2$ $TiCl_5$	$[SbEt_4]$ $TiCl_4$
1206	1211	1209	1205	1206	1206
1033	1034	1032	1032	1030	1030
996	996	991	984	996	993
966	970	969	966	952	967
—	—	784	797	—	—

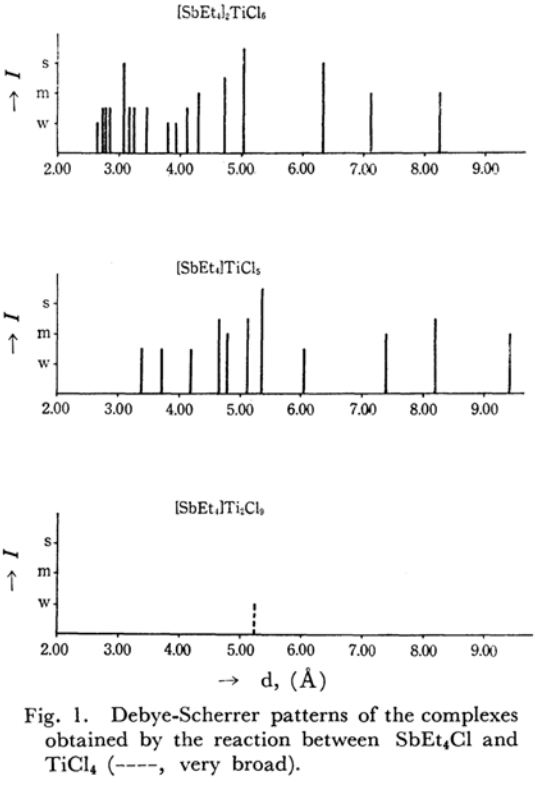

Fig. 1. Debye-Scherrer patterns of the complexes obtained by the reaction between $SbEt_4Cl$ and $TiCl_4$ (----, very broad).

Titanium Trichloride. The reaction of tetraethylstibonium chloride with titanium trichloride was carried out in a similar manner. Unreacted tetraethylstibonium chloride was removed from the solid product by extraction with benzene. The presence of unreacted titanium trichloride in the products was analyzed by powder X-ray diffractometry. The results of the reaction are summarized in Table 3. The products were proved, by the polarographic determination of the tetraethylstibonium ion and IR measurements, to be stibonium complex salts, as Table 3 shows. The main shifts of the IR absorptions from those of the analogous compounds are shown in Table 2. The powder X-ray diffraction patterns of the complexes are shown in Fig. 2. Both the 2 : 1 and the 1 : 1 complexes were highly crystalline.

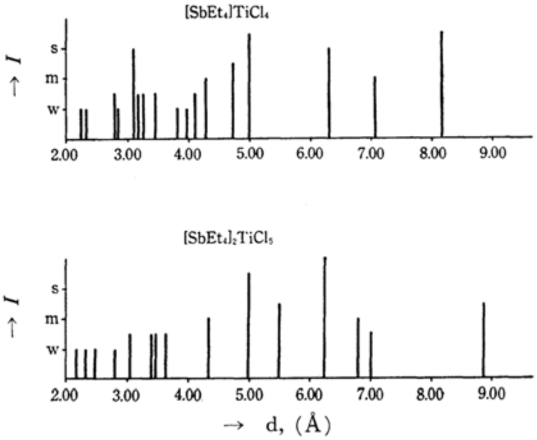

Fig. 2. Debye-Scherrer patterns of the complexes obtained by the reaction between $SbEt_4Cl$ and $TiCl_3$.

All the complexes dissolved in water and alcohols. They decomposed just under their melting points as follows: $[SbEt_4]_2TiCl_5$, 165—200°C (decomposed); $[SbEt_4]TiCl_4$, 200—204°C (decomp.). Attempts with a large number of solvents failed to recrystallize the complexes.

Titanium Dichloride. The reaction of tetraethylstibonium chloride with titanium dichloride was carried out in a stainless-steel pressure bottle in a similar manner. The reaction was mild at room temperature, but at a higher temperature of 80°C, a large amount of gas was evolved. The solid product was treated as before. The results of the reaction are summarized in Table 4. The gaseous products were found by gas chromatographic analysis to be an equimolar mixture of ethane and ethylene; the molar amount of the gaseous products nearly corresponded to that of titanium dichloride used for the reaction. The products agreed with the $TiCl_3(SbEt_4Cl)_n$ formula, where n was 1.5—1.9, and they were proved to be mixtures of the tetraethylstibonium complex salts, $[SbEt_4]_2TiCl_5$ (2 : 1 complex) and $[SbEt_4]TiCl_4$ (1 : 1 complex,) by X-ray analysis, a study of the IR spectra, and a polarographic determination of the tetraethylstibonium ion. Furthermore, tetraethylstibonium chloride was isolated nearly quantitatively from the hydrolyzates of these products.

Table 3. Reaction of tetraethylstibonium chloride with titanium trichloride

Temperature: 60°C, Time: 17−24 hr, Benzene 200 cc

Reactants		Yield g (Theor.)	Appearence	Benzene-insoluble product Analysis*						TiCl$_3$ unreacted	Postulated formula
SbEt$_4$Cl g	SbEt$_4$Cl/TiCl$_3$ mole ratio			Sb%	Ti%	Cl%	C%	H%	SbEt$_4^+$ %**		
114.0	2.50	120.0 (119.2)	Yellow crystals	32.66 (34.73)	6.27 (6.83)	24.87 (25.29)	27.57 (27.40)	5.57 (5.75)	60.53 (67.89)	(−)	[SbEt$_4$]$_2$TiCl$_5$
68.3	1.00	106.5 (106.9)	brown crystals	27.44 (28.47)	10.99 (11.20)	33.52 (33.16)	21.48 (22.46)	4.52 (4.71)	49.03 (55.64)	(−)	[SbEt$_4$]TiCl$_4$
20.5	0.50	43.7 (43.6)	brownish violet powder	—	—	—	—	—	—	(+)	[SbEt$_4$]TiCl$_4$ + TiCl$_3$

* Values in parentheses are calculated for the posturated formulas.

** Amounts of tetraethylstibonium ion detected in the hydrolyzates.

Table 4. Reaction of tetraethylstibonium chloride with titanium dichloride

Solvent: Benzene 100 cc

Reaction condition				Yield g	Appearence	Solid product insoluble in benzene Analysis						Postulated formula
TiCl$_2$ g	SbEt$_4$Cl/TiCl$_2$ mole ratio	Temp. °C	Time hr			Sb%	Ti%	Cl%	C%	H%	SbEt$_4^+$	
3.19	4.0	80	24	16.3	Yellowish brown powder	34.37 (1.86)	7.28 (1.00)	26.08 (4.83)	26.26 (Et:	5.64 7.20)	63.19 (1.75)	TiCl$_3$(SbEt$_4$Cl)$_{1.86}$
3.11	4.0	110	24	14.5	Yellow powder	32.78 (1.56)	8.25 (1.00)	27.64 (4.53)	25.46 (Et:	5.39 6.16)	58.07 (1.42)	TiCl$_3$(SbEt$_4$Cl)$_{1.56}$

* Values in parentheses are atomic or molar ratios.

TABLE 5. REACTION OF TRIETHYLANTIMONY DICHLORIDE WITH TITANIUM TETRACHLORIDE

Temperature: 60°C, Time: 15 hr

Reactants		Yield	Appearence	*n*-Hexane-insoluble product Analysis					Postulate formula
$SbEt_3Cl_2$ g	$SbEt_3Cl_2/TiCl_4$ mole ratio	g		Sb%	Ti%	Cl%	C%	H%	
33.60	2.00	35.3	Yellowish dark-brown liquid	31.46 (1.00)	6.79 (0.55)	38.27 (4.18)	18.16	3.87 (Et: 2.92)	$SbEt_3Cl_2\cdot(TiCl_4)_{0.55}$
16.80	1.00	25.3	Yellowish dark-brown liquid	27.06 (1.00)	9.73 (0.91)	42.40 (5.48)	16.80	4.01 (Et: 3.15)	$SbEt_3Cl_2\cdot(TiCl_4)_{0.91}$
16.80	0.50	31.3	Yellowish dark-brown liquid	24.27 (1.00)	11.80 (1.24)	46.90 (6.65)	14.15	2.72 (Et: 2.97)	$SbEt_3Cl_2\cdot(TiCl_4)_{1.24}$

* Values in parentheses are atomic or molar ratios.

TABLE 6. REACTION OF TRIETHYLSTIBINE WITH TITANIUM TETRACHLORIDE

Temperature: −25→20°C, Time: 2 hr, *n*-Hexane: 200 ml

Reactants		Yield	Appearence	*n*-Hexane-insoluble product Analysis*					Postulated formula
$SbEt_3$ g	$SbEt_3/TiCl_4$ mole ratio	g		Sb%	Ti%	Cl%	C%	H%	
20.9	0.20	58.5	Dark-brown powder	21.78 (0.53)	16.18 (1.00)	46.40 (3.88)	12.70	2.72 (Et: 1.57)	$TiCl_3(SbEt_3Cl_2)_{0.44}(SbEt_3)_{0.09}$
20.9	1.00	34.0	Dark-brown powder	23.22 (0.60)	15.21 (1.00)	39.77 (3.53)	14.26	3.00 (Et: 1.87)	$TiCl_3(SbEt_3Cl_2)_{0.27}(SbEt_3)_{0.33}$
83.6	4.00	28.5	Brown powder	28.19 (0.82)	13.52 (1.00)	34.04 (3.39)	16.79	3.67 (Et: 2.47)	$TiCl_3(SbEt_3Cl_2)_{0.20}(SbEt_3)_{0.62}$

* Values in parentheses are atomic or molar ratios.

Reactions of Triethylantimony Dichloride with Titanium Chlorides. *Titanium Tetrachloride.* The reaction was completed by keeping the reaction mixture in a sealed ampoule with shaking at 60°C for 15 hr under a nitrogen atmosphere. When poured into a large amount of *n*-hexane, the reaction mixture separated into two liquid layers. The lower layer was washed repeatedly with *n*-hexane to leave an insoluble liquid product. The material balance of the reaction and the analysis of the insoluble products are summarized in Table 5. The analytical values of the products agreed with the $SbEt_3Cl_2 \cdot (TiCl_4)_n$ formula, where n was 0.5—1.3; this result indicated the formation of two or more complexes. These products are thought to be mixtures of complexes, such as $(SbEt_3Cl_2)_2 \cdot TiCl_4$, $SbEt_3Cl_2 \cdot TiCl_4$, and $SbEt_3Cl_2 \cdot 2TiCl_4$. All the products showed the same IR spectra in the 650—4000 cm^{-1} frequency range. The spectra resembled that of triethylantimony dichloride, although a new absorption at about 775 cm^{-1} was observed and an absorption at 1405 cm^{-1} shifted to 1402 cm^{-1} in the complexes.

The reaction mixtures of triethylantimony dichloride and titanium tetrachloride showed remarkable electrical conductivities at room temperature. The variation in the specific conductance as a function of the reactant ratios is shown in Fig. 3. The minium conductance found in the equimolar mixture suggests that at least the 1 : 1 complex $SbEt_3Cl_2 \cdot TiCl_4$ has been formed.

Titanium Trichloride. The reaction of triethylantimony dichloride with titanium trichloride was carried out in a sealed ampoule at 60°C for 20 hr under a nitrogen atmosphere without using any solvent. The reaction proceeded with difficulty, and no appreciable change in the color of titanium trichloride was observed. The solid product was, after repeated washings with benzene, treated as before and analyzed. Only 1.06% of antimony was found to be combined with the solid product. The powder X-ray diffraction pattern of the product coincided with that of titanium trichloride.

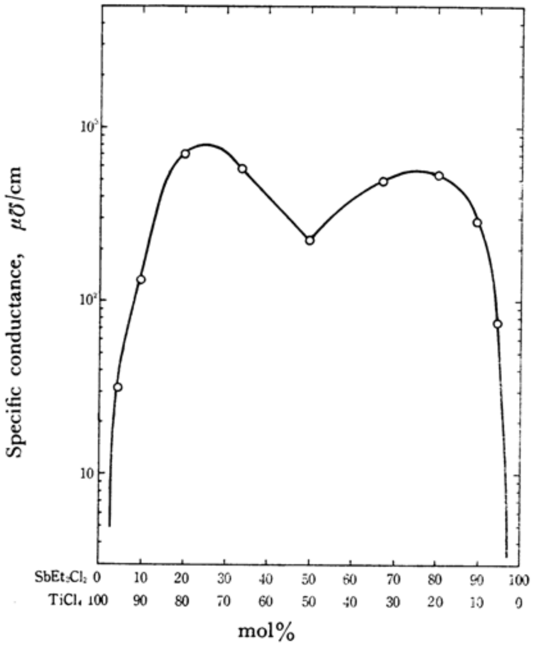

Fig. 3 Electrical conductivities of the mixtures of $SbEt_3Cl_2$ and $TiCl_4$.

Titanium Dichloride. The reaction of triethylantimony dichloride with titanium dichloride was carried out at 60°C for 48 hr in a manner similar to that described above. When an excess of triethylantimony dichloride was allowed to react, 8.78 g of titanium dichloride gave 22.5 g of a black solid product. The composition of the product was analyzed as follows: Found: Sb, 24.69; Ti, 15.96; Cl, 37.96; C, 15.07; H, 3.34%; Sb : Ti : Cl : Et = 0.61 : 1.00 : 3.21 : 1.88 atomic (mole) ratio. These values agreed with the $(TiCl_3)(SbEt_3)_{0.50} \cdot (SbEt_3Cl_2)_{0.11}$ formula. When hydrolyzed, the product liberated a nearly theoretical amount of triethylstibine, with a smaller amount of triethylantimony dichloride; these substances were identified by a study of their IR and NMR spectra. These results suggest that the complex is the simple adduct shown by the above formula.

The powder X-ray diffraction pattern of the product did not show the lines characteristic of titanium chlorides. This clearly shows the absence of unreacted titanium dichloride. However, the possibility of the presence of amorphous titanium trichloride with no coordinated alkylantimony ligand still remains.

Reactions of Triethylstibine with Tritanium Chlorides. *Titanium Tetrachloride.* Into a 500 cc round flask equipped with a dropping funnel, a magnetic stirrer, and a glass filter connected from the reaction flask to another round flask, an aliquot of titanium tetrachloride and 200 cc of *n*-hexane were placed. Triethylstibine diluted with 100 cc of *n*-hexane was added drop by drop with stirring at −25°C under a nitrogen atmosphere. After the addition, the temperature was raised to room temperature, and the stirring was continued a further 1.5 hr. The reaction mixture was then filtered using the connected glass filter, after which 100 cc of fresh *n*-hexane was added to the solid product which remained in the reaction flask. After having been stirred for several minutes, the solution was filtered off. Similar washings were repeated 10 times, and the solvent was evaporated under reduced pressure, leaving the solid product. All through the procedure oxygen and moisture were excluded strictly.

The results of the reaction are sumarized in Table 6. No gas evolution was observed during the reaction. When an excess of titanium tetrachloride was allowed to react, the analytical values of the product nearly agreed with $SbEt_3Cl_2 \cdot (TiCl_3)_2$. The yield was 99% assuming the following reaction:

$$2\,TiCl_4 + SbEt_3 \rightarrow SbEt_3Cl_2 \cdot 2\,TiCl_3 \qquad (3)$$

When hydrolyzed, the product gave a theoretical amount of triethylantimony dichloride, suggesting that the complex is a simple adduct of titanium trichloride with triethylantimony dichloride. The powder X-ray diffraction pattern of this product showed no characteristic line of titanium trichloride. However, it has not been clarified whether it is the 1 : 2 complex $SbEt_3Cl_2 \cdot 2TiCl_3$ or an equimolar mixture of the 1 : 1 complex $SbEt_3Cl_2 \cdot TiCl_3$ and titanium trichloride.

When equimolar or excess triethylstibine was allowed to react, the analytical values of the products agreed with the $TiCl_3 \cdot mSbEt_3Cl_2 \cdot nSbEt_3$. When hydrolyzed, the products liberated nearly theoretical amounts of triethylantimony dichloride and triethylstibine, which were identified by means of their IR and NMR spectra, suggesting that the complexes are simple adducts.

Titanium Trichloride and Titanium Dichloride. The reactions of triethylstibine with titanium trichloride and with titanium dichloride were attempted in a manner similar to that used in the reaction of titanium trichloride with triethylantimony dichloride. However, the reactions proceeded with difficulty, and no change in the appearance of the titanium chlorides was observed. The solid products contained only 1.15 and 0.88% of antimony respectively, and the powder X-ray diffraction patterns of the products coincided exactly with those of the starting titanium chlorides.

Discussion

The reactions of a series of ethylantimony compounds with titanium chlorides are summarized in Table 7. Table 7 shows that two types of reactions occur: (a) complex formation reactions, without any change in the valencies of the metals, and (b) redox reactions, followed by complex formations.

Complex Formations with No Change of the Metal Valencies. Tetraethylstibonium chloride reacts with titanium tetrachloride and with titanium trichloride to give a variety of tetraethylstibonium complex salts of quadrivalent and tervalent titanium chlorides respectively, according to the following equations:

$$SbEt_4Cl \text{ (in excess)} + TiCl_4 \rightarrow [SbEt_4]_2TiCl_6 \tag{4}$$

$$SbEt_4Cl + TiCl_4 \rightarrow [SbEt_4]TiCl_5 \tag{5}$$

$$SbEt_4Cl + TiCl_4 \text{ (in excess)} \rightarrow [SbEt_4]Ti_2Cl_9 \tag{6}$$

$$SbEt_4Cl \text{ (in excess)} + TiCl_3 \rightarrow [SbEt_4]_2TiCl_5 \tag{7}$$

$$SbEt_4Cl + TiCl_3 \rightarrow [SbEt_4]TiCl_4 \tag{8}$$

Triethylantimony dichloride also reacts with titanium tetrachloride to form the quadrivalent titanium complexes, $SbEt_3Cl_2{\cdot}nTiCl_4$, which have been proved by conductometric measurements to be ionic compounds.

Complex Formations Accompanied by Redox Reactions. The oxidation of titanium was observed in the reactions of titanium dichloride. Tetraethylstibonium chloride reacts with titanium dichloride to give complexes containing tervalent titanium, $[SbEt_4]_2TiCl_5$ and $[SbEt_4]TiCl_4$, with the evolution of an equimolar mixture of ethane and ethylene. The reaction seems to proceed as follows:

$$TiCl_2 + SbEt_4Cl \rightarrow TiCl_3 + SbEt_4\cdot \tag{9}$$

$$SbEt_4\cdot \rightarrow SbEt_3 + Et\cdot \tag{10}$$

$$2\,Et\cdot \rightarrow EtH + CH_2{=}CH_2 \tag{11}$$

The titanium trichloride which resulted from reaction (9) is considered to have formed the $[SbEt_4]_2TiCl_5$ and $[SbEt_4]TiCl_4$ complexes according to Eqs. (7) and (8) respectively.

Similar redox reactions occur between triethylantimony dichloride and titanium dichloride, forming mainly the tervalent titanium adducts $SbEt_3{\cdot}nTiCl_3$, where n is 2 or 1. Triethylantimony dichloride is reduced to triethylstibine, and titanium dichloride is oxidized to a tervalent state. Therefore, the coordination between these products may result in the formation of the above adducts. The reaction can be written as follows:

$$\begin{array}{c} 2\,TiCl_2 + SbEt_3Cl_2 \rightarrow 2\,TiCl_3 + SbEt_3 \\ \downarrow \\ SbEt_3\cdot 2\,TiCl_3 \text{ or } (SbEt_3\cdot TiCl_3 + TiCl_3) \end{array} \tag{12}$$

The reduction of titanium was observed in the reaction between triethylstibine and titanium tetrachloride. In the presence of excess titanium tetrachloride, the adduct $SbEt_3Cl_2{\cdot}nTiCl_3$, where n is 2 or 1, is obtained according to the following equation:

$$\begin{array}{c} 2\,TiCl_4 + SbEt_3 \rightarrow SbEt_3Cl_2 + 2\,TiCl_2 \\ \downarrow \\ SbEt_3Cl_2\cdot 2\,TiCl_3 \text{ or } (SbEt_3Cl_2\cdot TiCl_2 + TiCl_3) \end{array} \tag{13}$$

In the presence of excess triethylstibine, the further addition of triethylstibine to the adduct $SbEt_3Cl_2{\cdot}nTiCl_3$ occurs, accompanied by the displacement of the triethylantimony dichloride ligand by triethylstibine. The final product is represented as $TiCl_3{\cdot}mSbEt_3Cl_2{\cdot}nSbEt_3$.

TABLE 7. THE PRODUCTS FROM THE PEACTIONS OF ETHYLANTIMONY COMPOUNDS WITH TITANIUM CHLORIDES

	Antimony compound		
Titanium chloride	$SbEt_4Cl$	$SbEt_3Cl_2$	$SbEt_3$
$TiCl_4$	$[SbEt_4]_2TiCl_6$ $[SbEt_4]TiCl_5$ $[SbEt_4]Ti_2Cl_9$	$(SbEt_3Cl_2)_m(TiCl_4)_n$	$SbEt_3Cl_2\cdot nTiCl_3$ $TiCl_3\cdot mSbEt_3Cl_2\cdot nSbEt_3$ (Ti(IV) → Ti(III))
$TiCl_3$	$[SbEt_4]_2TiCl_5$ $[SbEt_4]TiCl_4$	difficult to react	difficult to react
$TiCl_2$	$[SbEt_4]_2TiCl_5$ $[SbEt_4]TiCl_4$ (Ti(II) → Ti(III))	$SbEt_3\cdot nTiCl_3$ (Ti(II) → Ti(III))	difficult to react

It is interesting to note that the complexes of titanium trichloride with triethylstibine and with triethylantimony dichloride can both thus be prepared starting from titanium tetrachloride. All attempts to prepare these complexes in an appreciable yield from the direct reactions of titanium trichloride with triethylstibine and with triethylantimony dichloride were unsuccessful. Only a very small amount of antimony compounds was found to be combined with titanium trichloride at 60°C. One may conclude that if any reactions occured, they were limited to the localized crystalline surface of the titanium trichloride.

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