$$4C(\text{graphite}) + 5H_2(g) + S(\text{rhombic}) = C_4H_{10}S(\text{liq})$$

	$\Delta Hf°_{298.16}$, kcal. mole^{-1}	$\Delta Sf°_{298.16}$, cal. deg.$^{-1}$ mole^{-1}	$\Delta Ff°_{298.16}$, kcal. mole^{-1}	$\log_{10} Kf_{298.16}$
1-Butanethiol	−29.61 ± 0.28	−103.16	+1.15	−0.84
2-Thiapentane	−28.03 ± .22	−103.98	+2.97	−2.18

The standard heat of vaporization, $\Delta H_v°_{298.16}$, was calculated by use of eq. 5, 6, 7, 9 and 10, the data of ref. 21, and the relationship, $\Delta Hv° = \Delta H_v - BRT/V + (dB/dT)\cdot RT^2/V$. The values obtained were 8.74 kcal. mole^{-1} for 1-butanethiol and 8.67 kcal. mole^{-1} for 2-thiapentane.

use of values of entropy from Table X and the thermodynamic functions for C(graphite),[8] $H_2(g)$[8] and S (rhombic).[25]

The foregoing values of the heat of vaporization were used to obtain the values of the standard heat of formation of the gas tabulated below. Also tabulated are values of the standard entropy, standard free energy and logarithm of the equilibrium constant of formation, calculated by use of values of entropy from Tables II and III.

$$4C(\text{graphite}) + 5H_2(g) + S(\text{rhombic}) = C_4H_{10}S(g)$$

	$\Delta Hf°_{298.16}$, kcal. mole^{-1}	$\Delta Sf°_{298.16}$ cal. deg.$^{-1}$ mole^{-1}	$\Delta Ff°_{298.16}$, kcal. mole^{-1}	$\log_{10} Kf_{298.16}$
1-Butanethiol	−20.87 ± 0.29	−79.44	+2.82	−2.06
2-Thiapentane	−19.36 ± .23	−80.28	+4.58	−3.35

The heat of formation of $S_2(g)$ from rhombic sulfur[9] was used to compute values of the heat of formation from $S_2(g)$, as given in Table I.

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[25] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," N. B. S. Circular 500, 1952, Series, 1, Table 14-1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Molecular Addition Compounds of Titanium Tetrabromide and Titanium Tetraiodide with Several Ethers

BY ROBERT F. ROLSTEN AND HARRY H. SISLER[1]

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The reactions of titanium tetrabromide and titanium tetraiodide with 1,4-dioxane, tetrahydrofuran and tetrahydropyran have been studied and the new compounds $TiBr_4\cdot O(CH_2CH_2)_2O$, $TiBr_4\cdot 2C_4H_8O$ and $TiBr_4\cdot 2C_5H_{10}O$ have been isolated. No pure addition compound of titanium tetraiodide with any one of the ethers could be isolated. It is believed that splitting of the ethers occurs in the presence of the tetraiodide and to some extent with the tetrabromide.

Introduction

Previous publications from this Laboratory[2-4] have shown that whereas tin and titanium tetrachlorides readily form stable, solid molecular addition compounds with various ethers, silicon and germanium tetrachlorides do not do so. The formation of tin tetrachloride addition compounds was interpreted as resulting from Lewis acid-base reactions in which the metal atom expanded its valence shell by accepting a pair of electrons from an oxygen atom of each of two molecules of ether to form compounds of the general type $MCl_4\cdot 2R_2O$. The failure of silicon and germanium tetrachlorides to form such compounds was attributed to the size of the chlorine atom being such as to cause four of these atoms to fill so completely the coördination sphere of the silicon and germanium atoms, as to prevent any reaction with the ether. This is in line with the measurements[5] of the dipole moments of solutions of silicon, germanium and tin tetrachlorides in dioxane, which indicate that the extent of coördination with the dioxane increases in the sequence $SiCl_4 < GeCl_4 > SnCl_4$.

It was decided, therefore, to determine the effect, if any, of the replacement of the chlorine atoms in titanium tetrachloride by larger halogens, on the tendency for titanium tetrahalides to react with ethers.

Experimental

Preparation and Purification of Materials.—Titanium used for preparing the tetrabromide and tetraiodide was prepared and purified by the method of Campbell, *et al.*,[6] and was shown spectroscopically to contain less than 0.1% metallic impurity. C.P. grades of bromine and iodine were used without further purification.

Titanium tetrabromide was prepared and purified by the method of Blocher and Rolsten[7] from pure titanium metal and liquid bromine and its purity checked by analysis. *Anal.* Calcd. for $TiBr_4$: Ti, 13.03; Br, 86.97. Found: Ti, 13.2, 13.1; Br, 86.8, 86.7.

Titanium tetraiodide was prepared by the direct reaction of gaseous iodine and excess titanium metal in the absence of air and moisture. It was purified by distillation and stored over P_4O_{10} in a desiccator. *Anal.* Calcd. for TiI_4: Ti, 8.62; I, 91.38. Found: Ti, 8.55, 8.71; I, 91.4, 89.0, 89.7.

The 1,4-dioxane was purified by the method of Fieser.[8] Tetrahydrofuran and tetrahydropyran were dried over calcium chloride, and then fractionated from over sodium in a dry argon atmosphere using a five-foot column packed with glass helices. A constant boiling middle fraction was retained. Boiling point data: C_4H_8O, 65.2–65.6° (743 mm.); 1,4-dioxane, 100.3–100.7° (744 mm.); $C_5H_{10}O$, 87.5–88.5° (746 mm.). The 1,4-dioxane froze at 11.57°. To avoid the presence of peroxides which these ethers form readily, they were prepared immediately before use.

Preparation of $TiBr_4\cdot C_4H_8O_2$.—Titanium tetrabromide was allowed to react with an excess of carefully dried 1,4-dioxane in a closed system under an atmosphere of dry argon. During the reaction the dioxane was kept at a tem-

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[1] Department of Chemistry, University of Florida, Gainesville, Florida.

[2] H. H. Sisler, W. J. Wilson, B. J. Gibbins, H. H. Batey, B. Pfahler and R. Mattair, THIS JOURNAL, **70**, 3818 (1948).

[3] H. H. Sisler, H. H. Batey, B. Pfahler and R. Mattair, *ibid.*, **70**, 3821 (1948).

[4] H. H. Sisler, P. M. Hamilton, R. McBeth and W. Bekebrede, *ibid.*, **75**, 2881 (1953).

[5] T. J. Lane, P. A. McCusker and B. C. Curran, *ibid.*, **64**, 2076 (1942).

[6] I. E. Campbell, R. I. Gaffee, J. M. Blocher, Jr., J. Gurland and B. W. Gonser, *Trans. Electrochem. Soc.*, **93**, [6] 271 (1948).

[7] J. M. Blocher and R. F. Rolsten, *ibid.*, in press.

[8] L. Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, Pt. II, p. 368, 1941.

perature just above its melting point (11.6°) and the rate of addition carefully controlled so as to control the highly exothermic addition reaction. The titanium tetrabromide was precooled to −78° at the start of the reaction. The addition compound forms very rapidly; some of it dissolves in the excess dioxane to yield a blood red liquid; the rest crystallizes as a red solid. The reaction mixture was subjected to considerable agitation to complete the heterogeneous reaction. A portion of the saturated supernatant solution was evaporated under vacuum to obtain a sample of the addition compound for analysis. During this process the system was carefully protected from moisture.

In Table I are found the analyses of five different preparations of the addition compound of tetrabromide with 1,4-dioxane. The analytical results compare quite favorably with the calculated values for the 1:1 addition compound.

TABLE I

CHEMICAL ANALYSIS OF $TiBr_4 \cdot 1,4$-DIOXANE

	Ti, %	Br, %	C, %	H, %
Theor. for $TiBr_4 \cdot 1,4$-dioxane	10.51	70.15	10.55	1.77
Prep. no. 1	10.31	69.92[a]	10.12	1.79
Prep. no. 2	...	68.7[b]	10.63	1.91
Prep. no. 3	...	69.9[b]	10.47	..
Prep. no. 4	10.51	69.6[b]	10.58	1.90
Prep. no. 5	10.74	69.5[b]	10.60	1.91

[a] Determined gravimetrically. [b] Determined volumetrically.

The addition compound is blood red in color, appreciably soluble in nitrobenzene and 1,4-dioxane, but insoluble in isoöctane, toluene and xylene. It does not have a sharp melting point but decomposes in the temperature range of 167–180°.

Preparation of $TiBr_4 \cdot 2C_5H_{10}O$ and $TiBr_4 \cdot 2C_4H_8O$.—The reaction at 0° between titanium tetrabromide and either tetrahydropyran or tetrahydrofuran results in the formation of a red solid and a wine colored liquid. The solid slowly dissolves and the wine colored liquid gradually darkens to a liquid which is dark red to black in color. When the pressure is reduced above the red to black liquid at 0° to remove the excess ether, no solid product is obtained, but rather a liquid of extremely high viscosity. Attempts to crystallize a solid from the liquid at −78° only further increased the viscosity.

Solid addition compounds were prepared as follows: an excess of the ether, cooled to 0°, was added to the tetrabromide at −78°. The reaction, which is highly exothermic, rapidly yields a deep red solid. The reaction mixture was allowed to stand and the supernatant liquid decanted. The solid was washed in the absence of moisture with freshly distilled ether until the wash liquid over the solid addition compound was colorless, indicating that the solid is not appreciably soluble in the ether and that the soluble impurity had been successfully removed. The clear liquid ether layer was then removed by decantation and evacuation. The vacuum drying process lasted for a period of 48 hours, at the end of which time the unit was pressurized to one atmosphere with dry argon. The product was stored in small weighing bottles in a desiccator over P_4O_{10}. The procedure just described involves the formation of the compound in the presence of excess base (ether).

To study the formation of the compound in excess acid (tetrabromide) the procedure was modified as follows. The ether was added to an excess of the tetrabromide at −78° and no liquid layer was obtained—only the red solid. The bulk of the uncombined tetrabromide was removed by reducing the pressure over the product to 1 mm. for two days. Final traces of unreacted tetrabromide were sublimed by raising the temperature to 40° for another seven days. At the outset of the process, the rate of removal of tetrabromide apparently was governed only by the sublimation pressure, but as time progressed, the rate of removal seemed to be determined by the rate of diffusion of tetrabromide vapor through the solid addition compound. All free tetrabromide was considered to have been removed when the small tube located between the bulb containing the solid compound and vacuum pump had no solid yellow tetrabromide condensed on the wall after being held at −78° for 48 hours. The solid addition compound was placed in weighing tubes which were stored in a desiccator over P_4O_{10}.

In Table II are found the analyses of two different preparations of the addition compound with tetrahydrofuran. These data support the formula $TiBr_4 \cdot 2C_5H_{10}O$.

TABLE II

CHEMICAL ANALYSIS OF $TiBr_4 \cdot 2C_5H_{10}O$

	Ti, %	Br, %	C, %	H, %
Theor. for $TiBr_4 \cdot 2C_5H_{10}O$	8.88	59.21	22.25	3.88
Prep. no. 1	9.00	58.62	22.71	4.00
Prep. no. 2	9.12	59.01	21.99	3.69

The brownish-red addition compound does not have a sharp melting point, but decomposes without melting. The red color of the solid turns a dark brown in the temperature range of 95–102° and this gradually deepens until a wine-colored liquid appears in the temperature range of 110–121°.

Table III gives the analyses of six different preparations of the addition compound $TiBr_4 \cdot 2C_4H_8O$. Preparations 1, 2, 3 were made in excess tetrahydrofuran, the others with excess tetrabromide. It is apparent from the agreement between the empirical and the theoretical percentages that the addition compound $TiBr_4 \cdot 2C_4H_8O$ is formed irrespective of whether the reaction takes place in excess tetrahydrofuran or excess titanium tetrabromide. The brownish-red addition compound is insoluble in carbon tetrachloride, chloroform and tetrahydrofuran.

TABLE III

CHEMICAL ANALYSIS OF $TiBr_4 \cdot 2C_4H_8O$

	Ti, %	Br, %	C, %	H, %
Theor. for $TiBr_4 \cdot 2C_4H_8O$	9.36	62.46	18.78	3.15
Prep. no. 1	9.73	64.55	18.30	3.72
Prep. no. 2	9.94	64.80	...	..
Prep. no. 3	9.57	64.62	19.77	3.88
Prep. no. 4	9.64	61.33	...	..
Prep. no. 5	9.74	61.33	19.20	3.44
Prep. no. 6	9.54	61.60	19.12	3.31

All attempts to isolate a pure product from the dark-colored liquid produced by the reaction of titanium tetrabromide and tetrahydrofuran at 0° failed, and the end product was a liquid of high viscosity. It is suspected that hydrogen bromide produced from the tetrabromide has caused the tetrahydrofuran ring to rupture yielding 4-bromobutanol-1, but this was not completely established. Infrared spectrograms of the liquid gave evidence of the presence of –OH groups.

Reaction of TiI_4 with 1,4-Dioxane.—Titanium tetraiodide and 1,4-dioxane react at 12° to form both a black liquid and a solid. This reaction is slightly exothermic. A jet black fluffy powder was obtained by using the procedure outlined above for the reaction of titanium tetrabromide with 1,4-dioxane. This fluffy powder did not give an X-ray powder diffraction pattern; this is characteristic of an amorphous powder. Quantitative analysis of different preparations of the powder for carbon, hydrogen, titanium and iodine were internally consistent but mutually inconsistent.

Reaction of TiI_4 with Tetrahydrofuran.—Titanium tetraiodide and tetrahydrofuran reacted at 0° to yield a red liquid and a solid which slowly became dark on storage under the red tetrahydrofuran liquid layer. Removal, by reduced pressure, of the excess solvent tetrahydrofuran, resulted in the formation of a very viscous red liquid from which we did not succeed in obtaining a solid, and which contained Ti and I in an approximately 1:3.5 ratio. The infrared spectrogram of the viscous liquid showed the presence of a strong (–OH) absorption band.

Discussion and Conclusions

Three solid addition compounds of titanium tetrabromide with ethers have been prepared and isolated. The corresponding addition compounds with titanium tetraiodide were not obtained. It is also to be noted[9] that $SnCl_4$ and $SnBr_4$ react with

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(9) H. H. Sisler, E. E. Schilling and W. O. Groves, THIS JOURNAL, **73**, 426 (1951).

both tetrahydrofuran and tetrahydropyran whereas SnI_4 appears to be inert.

The fact that titanium tetrachloride and bromide form stable addition compounds whereas the halides of germanium and silicon do not may be the result of the somewhat larger size of the titanium atom. Not to be overlooked, however, is the electronic configuration of the titanium atom which enables it to form very strong and stable hybrid orbitals of the "inner orbital" type, d^2sp^3. The configurations of germanium and silicon would require the less strongly bond-forming "outer orbital" sp^3d^2 hybrids.

Titanium tetrabromide and titanium tetraiodide react with tetrahydrofuran to form a viscous liquid which contains 1 mole of titanium to about 3.5 moles of halogen. Thus, some ionic bromine or iodine is lost as a result of the reaction. This did not occur[9] in the reaction between titanium tetrachloride and tetrahydrofuran. This behavior can be due to the partial hydrolysis of the tetrahalide with the formation of a hydrohalogen acid and the subsequent cleavage of the ether to form a 4-halobutanol-1. This conclusion is further substantiated by the presence of the strong (–OH) absorption band in the infrared spectrum. It is a well known fact that the acid strength[10] decreases in the series HI > HBr > HCl, and that tendency to cleave ethers decreases in the same sequence. Thus, one would not expect to encounter ring cleavage of the ether when working with a metal tetrachloride, whereas it might be expected when working with a metal tetraiodide or tetrabromide.

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(10) G. H. Richter, "Textbook of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 91.