boron trifluoride. The line was connected through a Housekeeper seal to a liquid nitrogen trap.

Most of the runs were initiated at room temperature; the magnesium and titanium nitrides required heating to 100° before reaction occurred. From 5 to 10 g. of the nitride was placed in a nickel boat and the reaction induced by passing fluorine into the system. Nitrogen or helium gas was used as a diluent in some cases, but each of the nitrides was allowed to react with undiluted fluorine at least once.

The molecular weights of the volatile products were calculated from gas density measurements. The products were identified by means of infrared spectroscopy by comparison with known samples (NF_3 and N_2O) and from reference spectra.

Results

All of the substances fluorinated gave predominantly nitrogen as a volatile product. No nitrogen trifluoride was observed in the case of the metallic type nitrides, TiN and VN. Small quantities of nitrogen trifluoride were observed in the other experiments. Nitrous oxide and carbon tetrafluoride were detected in all of the runs as the result of impurities in the fluorine and possibly in the nitrides. An estimate of the nitrogen trifluoride content of the product gas was obtained from the intensity of the absorption at 907 cm.$^{-1}$. The results are listed in Table I.

TABLE I

NITROGEN TRIFLUORIDE CONTENT OF PRODUCT GASES

Substance fluorinated	% NF_3	Substance fluorinated	% NF_3	Substance fluorinated	% NF_3
Li_3N	0.01	BN	0.01	Cu_3N	0.01
Li_3N	0.1	Si_3N_4	0.03	NH_4F	0.6
Bi_3N_2	0.2	Si_3N_4	0.3	NH_4F	0.01
Mg_3N_2	0.06	TiN	0.00	$N_2H_6F_2$	0.03
		VN	0.00	$N_2H_6F_2$	0.04

In all cases studied the reactions were too vigorous to permit the production of large amounts of nitrogen trifluoride.

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The Preparation of $M^I_2TiCl_6$ Compounds in Fused Antimony(III) Chloride

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The preparation of compounds of the type $M^I_2TiCl_6$ (M^I = K, Rb, Cs, NH_4) has been described in the literature.[1-9] These salts can be obtained by precipitation from aqueous hydrochloric acid–titanium tetrachloride solutions on addition of the corresponding alkali chloride,[1-6] by reaction of the solid alkali metal chloride with gaseous $TiCl_4$ at elevated temperatures (410°),[7-8] or, in some cases, by the reaction of $TiCl_4$ with the molten alkali metal chlorides.[9] The preparation of pure compounds from aqueous solutions is difficult because of the tendency of hexachlorotitanates to hydrolyze. The other methods have the disadvantage that hexachlorotitanates are not entirely stable at elevated temperatures. An attempt to prepare ammonium hexachlorotitanate by using aprotic solvents (thionyl chloride, etc.)[10] had only limited success, presumably because of the low solubility of ammonium chloride in these solvents.

Therefore it seemed advantageous to prepare compounds of this type by reactions of the dissolved monovalent metal chloride with $TiCl_4$ in a fused "semisalt" at relatively low temperatures (<100°). A suitable nonaqueous solvent system for this type of reaction is fused antimony trichloride. Many monovalent metal chlorides are easily soluble in this solvent,[11] and also $TiCl_4$ shows a good solubility in antimony trichloride melt. Hexachlorotitanates (*e.g.*, K, Rb, Tl) are insoluble in the melt. After reaction, the solidified $SbCl_3$ can be removed at room temperature with an organic solvent, which does not dissolve the hexachlorotitanate. Potassium hexachlorotitanate(IV) and thallium(I) hexachlorotitanate(IV) were prepared by this technique. Some properties of the thallium(I) salt are described.

Experimental

A known amount of KCl or TlCl ($\approx$1 g.) was dissolved in approximately 30 g. of double-distilled $SbCl_3$ in a Pyrex tube. After solidification of this mixture, $TiCl_4$ was added (10% more than required for the stoichiometric reaction $2MCl + TiCl_4$). The $TiCl_4$ was frozen by using a Dry Ice–acetone mixture, and the tube was sealed under vacuum. The sealed tube was heated to approximately 90° for 2 hr. and shaken from time to time. Then the tube was cooled to room temperature and broken, and its contents were transferred into a Soxhlet apparatus where the excess $TiCl_4$ and the solvent $SbCl_3$ were extracted with distilled dry CS_2. The remaining salt was dried from CS_2 in a vacuum desiccator over silica gel.

All chemicals used were of reagent grade purity. Because of the hygroscopic nature of the prepared substances, all operations were performed under a flow of dry nitrogen or in a drybox. The X-ray patterns of the thallium(I) hexachlorotitanate were obtained by using a 11.4-cm. diameter Philips powder came with Cu Kα radiation.

Results and Discussion

The salts K_2TiCl_6 and Tl_2TiCl_6 were prepared by using fused $SbCl_3$ as the solvent. The yields were 100% with respect to the dissolved KCl and TlCl. Both compounds obtained were yellow crystalline powders (the K salt was bright yellow and the Tl salt greenish yellow). *Anal.* Calcd. for K_2TiCl_6: K, 23.08; Ti, 14.14; Cl, 62.78. Found: K, 23.1; Ti, 14.2; Cl,

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TABLE I

hkl, RELATIVE INTENSITIES (I/I_0), AND INTERPLANAR SPACINGS OF Tl_2TiCl_6

hkl	I/I_0	*d*, Å.	*hkl*	I/I_0	*d*, Å.
111	3	5.64	642	5	1.314
200	8	4.90	800	1	1.225
220	10	3.48	733	1	1.186
311	<1	2.95	822	2	1.157
222	10	2.84	662	3	1.126
400	9	2.45	840	3	1.097
420	6	2.194	911	<1	1.072
422	7	2.004	664	1	1.047
440	7	1.738	844	2	1.003
531	<1	1.660	933	<1	0.9890
600	4	1.638	10 2 0	2	0.9638
620	5	1.554	951	1	0.9455
622	6	1.480	953	<1	0.9083
444	4	1.418	10 4 2	<1	0.8958
711	2	1.363	880	<1	0.8688

62.7. Calcd. for Tl_2TiCl_6: Tl, 61.08; Ti, 7.16; Cl, 31.76. Found: Tl, 61.2; Ti, 7.2; Cl, 31.6.

The properties of the potassium salt agreed with the findings of Schossberger[6] and Flengas.[7]

Engel[2] reported that the thallium salt could not be obtained from aqueous solutions. Morozov and Toptygin[9] prepared the thallium salt from aqueous solutions without giving details about the preparation.

We found that the thallium salt is stable in dry air and decomposes slowly in moist air (relative humidity $\approx 60\%$) at room temperature. The thallium(I) hexachlorotitanate is not soluble in water; after a few minutes it is hydrolyzed as indicated by the color change from yellow to white. The X-ray diffraction pattern of Tl_2TiCl_6 showed that the compound is isomorphous with Tl_2PtCl_6. The interplanar spacings, estimated relative intensities, and *hkl* values of the X-ray diffraction pattern of Tl_2TiCl_6 are listed in Table I. Its crystal structure is face-centered cubic with a space group $O^5{}_H$-Fm3m. There was some difficulty in accurately measuring the back reflection lines of the X-ray diagram because of their relatively low intensity and broadening. This was probably caused by the small crystallite size or crystal defects of the prepared compounds. The lattice constant, a_0, was calculated as the average from all *d* values neglecting the lines with $2\theta < 45°$. The lattice constant was found to be $a_0 = 9.804 \pm 0.008$ Å. This value is slightly higher than Engel predicted ($a_0 = 9.793$ Å.).[2]

The formation of K_2TiCl_6 and Tl_2TiCl_6 in fused $SbCl_3$ can be considered an acid–base reaction between the "base" KCl or TlCl and the "acid" $TlCl_4$ in the solvent $SbCl_3$. $TiCl_4$ behaves probably as a "Lewis acid" in fused $SbCl_3$. Another type of acid–base reaction in fused $SbCl_3$ was described by Jander and Swart.[11]

Preliminary experiments showed that by choice of suitable compounds and "semisalt" solvent systems, it was possible to prepare other hexahalotitanates which are either not or difficultly accessible by the methods mentioned above. The results of these investigations will be published later.

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Studies on the Synthesis and Crystal Structure of 1,4-Selenothiane

BY J. D. MCCULLOUGH AND PHILLIP RADLICK

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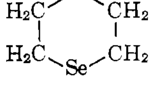
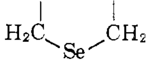
The synthesis of 1,4-selenothiane (I) was first reported by Gibson and Johnson.[1] These authors obtained I in "small yield" from the reaction of β,β'-dichlorodiethyl sulfide (mustard gas) on aqueous sodium selenide after unsuccessful attempts to obtain the desired product from the reaction of β,β'-dichlorodiethyl selenide (selenium mustard) with aqueous sodium sulfide. The poor yield in the one case and the failures in the other probably were due to the inability of Se^{-2} and S^{-2} to compete favorably with water in reacting with the cyclic sulfonium and selenonium ions, respectively.[2,3] In contrast, Johnson and Gibson obtained good yields of 1,4-selenoxane (II)[4] from the reaction of β,β'-dichlorodiethyl ether with aqueous sodium selenide. In this case the reaction path does not appear to involve a cyclic oxonium ion and Se^{-2} is able to compete favorably with water in replacing chlorine. It occurred to the present authors that the yield of 1,4-selenothiane might be greatly improved if β,β'-dichlorodiethyl sulfide and sodium selenide were brought together in a nonaqueous medium. The present note describes an improved synthesis of I based on this hypothesis and presents the results of a preliminary X-ray diffraction study of single crystals of the solid.



I



II

Experimental

Synthesis of 1,4-Selenothiane.—Sodium (4.6 g., 0.20 g.-atom) was dissolved in absolute ethanol (450 ml.) in a 1-l. flask equipped with a mercury-sealed stirrer, reflux condenser, gas dispersion tube, and dropping funnel. By means of a stream of nitrogen, the hydrogen selenide prepared by the action of water on aluminum selenide[5] (18 g., 0.062 mole) was passed into the alcoholic solution while the latter was being stirred. To the resulting brown solution, still under nitrogen gas, β,β'-dichlorodiethyl sulfide (15 g., 0.094 mole) in absolute ethanol (200 ml.) was added dropwise, with stirring, over a period of 10 min. The mixture was refluxed 2 hr., yielding a white precipitate. The mixture was then cooled, the solid was filtered off and washed with ether, and the washings were added to the filtrate. The

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