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## Synthesis of Ethoxytitanium(IV) Fluorides

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Alkoxytitanium chlorides and bromides of the form $TiX_n(OR)_{4-n}$ are known where R ranges from methyl to hexyl and $n = 1, 2,$ and 3.[2,3]

Molecular weight measurements on the tetraalkoxy and chlorotrialkoxy titanium(IV) compounds in benzene solution indicate molecular association leading to dimers and trimers. A number of structures have been proposed for these aggregates,[2,4,5] but no definitive structural data are available.

Fluorides of the general formula $Ti(OR)_3F$ are reported by Brucker[6] where R is an ethyl, isopropyl, or butyl group. The dialkoxy and monoalkoxy compounds have not been prepared. The preparations of the compounds $Ti(OC_2H_5)_2F_2$ and $Ti(OC_2H_5)F_3$ are reported herein. The following general equations describe reactions carried out in benzene which were utilized for synthesis

$$n\text{Ti(OR)}_4 + n\text{TiF}_4 \longrightarrow [\text{TiF}_2(\text{OR})_2]_{2n}$$

$$n\text{Ti(OR)}_4 + 3n\text{TiF}_4 \longrightarrow [\text{TiF}_3\text{OR}]_{4n}$$

### Experimental

**Materials.**—Titanium tetrafluoride supplied by the General Chemical Division of Allied Chemical and Dye Corporation was used without further purification.

Tetraethyl titanate was prepared by a reported procedure.[7]

**Triethoxytitanium(IV) Fluoride.**—In all synthetic procedures, glassware was carefully dried and all transfers of liquids were effected in a drybox. To a slurry containing 0.016 mole of $TiF_4$ in 25 ml. of benzene was added 0.05 mole of $Ti(OC_2H_5)_4$ in 25 ml. of benzene. The $TiF_4$ dissolved on stirring. It was found that addition of 5.06 g. (0.64 mole) of pyridine to the system minimized formation of the mono- and diethoxy fluorides. After refluxing the system for 24 hr., the clear, colorless solution was filtered and the solvent removed to give a white solid consisting of crude $TiF(OC_2H_5)_3$. The crude product was dissolved in 25 ml. of benzene and flooded out by adding petroleum ether. The resulting crystalline product is very sensitive to moisture and melted at 143–144°.

*Anal.* Calcd. for $TiF(OC_2H_5)_3$: C, 35.60; H, 7.42; Ti, 23.75; $OC_2H_5$, 66.80; F, 9.4. Found: C, 34.01; H, 7.42; Ti, 23.69; $OC_2H_5$, 66.54; F, 9.5.

The monofluoride was also obtained in pure form from a reaction in which pyridine was not added, by recrystallizing the crude product from a limited amount of benzene. In this study, we obtained a much better product using the above procedure than that prepared by the method of Brucker[6] using $Ti(OC_2H_5)_4$ and acetyl fluoride. The product prepared by the latter procedure melted at 110° and analysis indicated it is a mixture containing appreciable amounts of $TiF_2(OC_2H_5)_2$.

TABLE I
MOLECULAR WEIGHT DETERMINATIONS

| Compounds | Mole % | F.p. lowering | Mol. wt. | Calcd. mol. wt. of monomer |
|---|---|---|---|---|
| $Ti(OC_2H_5)_4$ | 0.20 | 0.10 | 300 | 228 |
| $Ti(OC_2H_5)_4$ | 2.00 | 0.460 | 666 | |
| $TiF(OC_2H_5)_3$ | 0.081 | 0.053 | 205 | 202 |
| $TiF(OC_2H_5)_3$ | 1.00 | 0.169 | 808 | |
| $TiF_2(OC_2H_5)_2$ | 0.113 | 0.018 | 727 | 176 |
| $TiF_3(OC_2H_5)$ | 0.088 | 0.010 | 868 | 150 |

**Diethoxytitanium(IV) Fluoride.**—An equimolar mixture (0.049 mole) of $TiF_4$ and $Ti(OC_2H_5)_4$ in 50 ml. of benzene was treated as described above except that pyridine was not added. The brittle, tan solid obtained upon solvent evaporation hydrolyzed rapidly when exposed to the atmosphere and melted at 115°. Redissolving in benzene followed by reprecipitation with petroleum ether produced a solid which also melted at 115°.

*Anal.* Calcd. for $TiF_2(OC_2H_5)_2$: C, 27.30; H, 5.68; Ti, 27.30; $OC_2H_5$, 51.10. Found: C, 26.84; H, 5.95; Ti, 27.69; $OC_2H_5$, 49.72.

**Ethoxytitanium(IV) Trifluoride.**—A mixture of $Ti(OC_2H_5)_4$ (0.0263 mole) and $TiF_4$ (0.077 mole) in benzene was treated as described above. The glass-like solid which remained after removal of solvent was reprecipitated from benzene with petroleum ether. The solid did not melt, but decomposed at 215°.

*Anal.* Calcd. for $TiF_3OC_2H_5$: C, 16.00; H, 3.33; Ti, 32.00. Found: C, 14.88; H, 3.61; Ti, 32.51.

**$Ti_3F_4(OC_2H_5)_8$.**—In several instances in this work compounds were obtained either as intermediates or products which were all similar in properties and correspond to the formula $Ti_3F_4(OC_2H_5)_8$. Brucker[6] has observed that stable addition compounds can be formed between triethyl antimonate and triethoxytitanium fluoride. The compound $Sb(OC_2H_5)_3 \cdot 3TiF(OC_2H_5)_3$ was characterized. Using a similar approach we were able to prepare the analogous titanium compound. A mixture of $TiF_4$ and $Ti(OC_2H_5)_4$ in a 1:2 ratio was refluxed for 24 hr. in 50 ml. of benzene, cooled, and filtered. Removal of the benzene at reduced pressure gave a white compound which melted at 132–135°. Recrystallization from benzene gave a material with a melting point of 135–136°.

*Anal.* Calcd. for $Ti_3F_4(OC_2H_5)_8$: C, 33.10; H, 6.90; Ti, 24.85. Found: C, 32.19; H, 6.72; Ti, 24.57.

Successive distillations of this compound resulted in a series of compounds, each of which came closer to pure $TiF(OC_2H_5)_3$ in analysis and melting point. The final compound was $TiF(OC_2H_5)_3$ which had a melting point of 146°.

*Anal.* Calcd.: C, 35.60; H, 7.42. Found: C, 35.79; H, 7.58.

**Molecular Weight Determinations.**—The molecular weight studies on benzene solutions of the compounds synthesized indicate (Table I) that in all cases except for very dilute triethoxytitanium fluoride solutions, aggregates of three or greater are formed.

## Discussion

Since $TiF_4$ is extensively polymerized in the solid state it is tempting to speculate that fluoride is a more effective bridging group in this system than ethoxide. As the amount of fluoride in the products is increased a definite increase in molecular weight occurs.

This conclusion receives support from an infrared investigation of the products and of solutions of tetraethyl titanate. The most recent report[8] on the infrared spectrum of tetraethyl titanate assigns the absorption

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band at 1100 cm.$^{-1}$ to bridging ester groups. This is in contrast to assignments made in previous work.[9,10] Absorption bands in the 1000 to 1150 cm.$^{-1}$ region are found at 1137, 1106, 1067, and 1045 cm.$^{-1}$. In this study, the intensity of the 1045 cm.$^{-1}$ band is found to be concentration dependent and practically disappears in dilute solution where the principal species is monomer. When wet solvent is employed the 1100 cm.$^{-1}$ band disappears. This finding supports the assignment of the 1045 cm.$^{-1}$ band to bridging ester groups. The infrared spectrum of the monofluoride, $TiF(OC_2H_5)_3$, also contained a band around 1045 cm.$^{-1}$ which disappeared on dilution. The solid, Nujol mull of $TiF_2(OC_2H_5)_2$ had a band at 1045 cm.$^{-1}$ but the spectrum of the solid compound $TiF_3OC_2H_5$ did not. The latter compound is probably completely fluorine-bridged.

There are a great number of structures which can be drawn for these compounds which preserve octahedral coordination about the titanium and allow a preference for fluorine *vs.* ethoxyl bridges. No conclusions regarding structure can be drawn.

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## Compounds of Post-Transition Elements with the Ordered Perovskite Structure[1]

BY ARTHUR W. SLEIGHT AND ROLAND WARD

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The preparation and characterization of numerous compounds of the formula $A_2BB'O_6$ having the ordered perovskite structure have been described in previous publications.[2-8] Since A is an alkaline earth cation, the sum of the oxidation states of B and B′ must be eight.

Except for Pb, Bi, Sn, and the group IIIb elements, post-transition elements have not been found in the perovskite structure as cations. Ordered perovskites containing Sb, Te, I, and Tl have now been prepared and are listed in Table I. Furthermore, the compound $Ba_2AgIO_6$ represents the first instance of Ag as a B cation in the perovskite structure. The color of $Ba_2InSbO_6$ suggests that this compound may be oxygen-deficient. It is assumed that many other analogous compounds may exist, but attempts to prepare compounds containing $Br^{VII}$, $Se^{VI}$, or $As^{V}$ as B cations were not successful.

TABLE I

$A_2BB'O_6$ TYPE COMPOUNDS

| Compound | Lattice constants<br>a, Å. | <br>c, Å. | Color |
|---|---|---|---|
| $Ba_2ScSbO_6$ | 8.197 | | White |
| $Ba_2InSbO_6$ | 8.269 | | Black |
| $Sr_2CrSbO_6$ | 7.862 | | Brown |
| $Sr_2FeSbO_6$ | 7.916 | | Pale green |
| $Sr_2GaSbO_6$ | 7.84 | 7.91 (tet.) | White |
| $Ba_2MgTeO_6$ | 8.13 | | Yellow |
| $Ba_2CaTeO_6$ | 8.393 | | Yellow |
| $Ba_2NaIO_6$ | 8.33 | | White |
| $Ba_2AgIO_6$ | 8.46 | | Brown |
| $Ba_2TlTaO_6$ | 8.42 | | Black |

### Experimental

Most of the reagents have been previously described.[3,6] $HIO_4 \cdot 2H_2O$, $NaIO_4$, $Sb_2O_3$, and $TeO_2$ were C.P. or reagent grade. $Tl_2O_3$ (99.2%) was obtained from K and K Laboratories, Inc. $Ag_2O$ was obtained from Merck and Co., Inc. In general, high temperature solid state reactions, indicated by the following equations, were used to prepare these compounds. The reactants were intimately mixed and fired in air.

$$4BaO_2 + B_2O_3 + Sb_2O_3 \xrightarrow{1100°} 2Ba_2BSbO_6 + O_2$$

$$B = \text{Sc or In}$$

$$4SrO + B_2O_3 + Sb_2O_3 + O_2 \xrightarrow{1100°} 2Sr_2BSbO_6$$

$$B = \text{Cr, Fe or Ga}$$

$$2BaO_2 + BO + TeO_2 \xrightarrow{1100°} Ba_2BTeO_6 + {}^1/{}_2O_2$$

$$B = \text{Mg or Ca}$$

$$2BaO + NaIO_4 \xrightarrow{400°} Ba_2NaIO_6$$

$$4BaO_2 + Tl_2O_3 + Ta_2O_5 \xrightarrow{1000°} 2Ba_2TlTaO_6 + 2O_2$$

$Ba_2NaIO_6$ could also be precipitated from a solution of $NaIO_4$ upon the addition of a $Ba(OH)_2$ solution. $Ba_2AgIO_6$ was prepared in a similar manner. A solution of $Ba(OH)_2$ was added to a slurry of $Ag_2O$ in a solution of periodic acid. All the ingredients were in stoichiometric proportions. The resulting slurry was digested on a steam bath for 12 hr. The product was filtered off and dried at 90°. $Ba_2AgIO_6$ could not be prepared by high temperature reactions due to the reduction of $Ag^I$ to Ag metal.

Analysis of these compounds was not carried out since no purification procedure was found. The diffraction patterns of the final products, however, were completely indexable on the basis of the parameters listed in Table I. The relative intensities of the reflections corresponded to the expected values for the ordered perovskite structure and in all cases the (111), (311), and (331) reflections due to the ordered structure were prominent.

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## Reactions of Some Chlorophosphines with Tributylphosphine

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We wish to report three interesting reactions in which tri-*n*-butylphosphine extracts chlorine atoms from various chlorophosphines to form products con-