

lamp and the reaction vessel, which remained connected to a vacuum gage during the irradiation and was cooled by an air blower. After about 6 hr., the pressure had dropped to the theoretical value and the reaction mixture was separated by pumping on it at  $-183^\circ$ , thus removing excess  $\text{OF}_2$ . No further purification of the product was necessary.

**Reaction of  $\text{SO}_3$  with  $\text{OF}_2$  without a Filter.**—Using the same vacuum apparatus 0.145 g. (0.0018 mole) of  $\text{SO}_3$  was transferred into a 1-l. Pyrex flask resulting in about 40 mm. pressure. Then,  $\text{OF}_2$  was added, bringing the total pressure to approximately 650 mm. The mixture was irradiated for 45 min. with ultraviolet light, transferred *in vacuo* to an n.m.r. tube,<sup>7</sup> and dissolved in a threefold excess of trichlorofluoromethane. A  $\text{F}^{19}$  n.m.r. analysis (Varian Model V-4302 spectrometer) of the mixture showed very small doublets at  $\delta_{\text{CCl}_3\text{F}} = -291$  and  $-43$  p.p.m., indicating the presence of a minute amount of I. The mixture also showed strong signals at  $-48.5$  and  $-33.5$  p.p.m. which were assigned to II and III, respectively.

**Reaction of  $\text{SO}_2$  and  $\text{OF}_2$ .**—With the same apparatus used above, 0.54 g. (0.01 mole) of  $\text{OF}_2$  and 0.64 g. (0.01 mole) of  $\text{SO}_2$  (Matheson Co.) were condensed into a 1-l. Pyrex flask resulting in a 170 mm. partial pressure of each component at room temperature. It was exposed to ultraviolet radiation at room temperature for 18 hr. The reaction mixture was then separated by bulb-to-bulb fractionation and yielded 0.566 g. (0.0031 mole = 62%) of pyrosulfuryl fluoride and a small portion of sulfuryl fluoride. Pyrosulfuryl fluoride was identified by its infrared spectrum<sup>8</sup> and by comparing its  $\text{F}^{19}$  n.m.r. spectrum with that of a sample which was prepared by another method.<sup>9</sup> The  $\text{F}^{19}$  spectrum consists of a signal at  $\delta_{\text{CCl}_3\text{F}} = -48.5$  p.p.m. Sulfuryl fluoride was identified by its infrared spectrum<sup>10</sup> and its  $\text{F}^{19}$  n.m.r. spectrum which showed a single signal at  $\delta_{\text{CCl}_3\text{F}} = -33.5$  p.p.m.

**Reaction of Peroxydisulfuryl Difluoride<sup>11</sup> with  $\text{OF}_2$ .**—A 2-l. Pyrex flask was filled with IV (purity monitored by infrared analysis) at a pressure of 60 mm. using a Pyrex glass vacuum apparatus; then  $\text{OF}_2$  was added until the total pressure was 200 mm. and the mixture was irradiated for 6 hr. at room temperature with a 360-watt high pressure mercury ultraviolet lamp. After a crude bulb-to-bulb distillation, the middle fraction was further separated by fractional codistillation<sup>12</sup> and consisted of silicon tetrafluoride, sulfuryl fluoride, fluorine fluorosulfonate (V), and peroxydisulfuryl difluoride. The latter was identified by its infrared spectrum, which showed peaks at 6.7, 8.0 (S-O stretch), 11.7 (S-F stretch), 12.7, and 13.8  $\mu$ , as well as by  $\text{F}^{19}$  n.m.r. spectroscopy. The compound showed two doublets at  $\delta_{\text{CCl}_3\text{F}} = -291$  and  $-43$  p.p.m. with a coupling constant  $J_{\text{FF}} = 10.5$  c.p.s. These spectra were identical with those of the compound made according to Schumacher.<sup>1</sup> Mass spectra were obtained with a Consolidated Electrodynamics Corporation Model 21-102 mass spectrometer, with an ionizing current of 52.2  $\mu$ a. and an ionizing potential of 70 volts. The spectrum showed major peaks corresponding to  $\text{SO}_3\text{F}^+$ ,  $\text{SO}_2\text{F}^+$ ,  $\text{SO}_3^+$ ,  $\text{FSO}^+$ ,  $\text{SO}_2^+$ ,  $\text{SF}^+$ ,  $\text{SO}^+$ , and  $\text{OF}^+$  and a number of minor peaks. The parent peak at mass number 134 was missing in all spectra.

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## The Fluorination of Nitrides

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Moissan<sup>2</sup> observed the reactions of the nitrides of boron and titanium with elementary fluorine but did not characterize the volatile products. Coates, Harris, and Sutcliffe<sup>3</sup> reported that boron trifluoride and nitrogen were the products of the direct fluorination of boron nitride. They also stated that magnesium nitride did not react with fluorine even at  $400^\circ$ . Glemsler and Haesler<sup>4</sup> obtained boron trifluoride and nitrogen from the reaction of boron nitride with fluorine and with silver(II) fluoride.

Ruff and Geisel<sup>5</sup> reported that fluorine did not react with ammonium fluoride or ammonium bifluoride.

Following a plan of study of the reactions of fluorine with carbides, previously reported,<sup>6</sup> the fluorination of a variety of types of nitrides was carried out to determine if any observable relationship exists between the structure possessed by a given nitride and the formation of nitrogen trifluoride as one of the products of its direct fluorination. Lithium nitride ( $\text{Li}_3\text{N}$ ), beryllium nitride ( $\text{Be}_3\text{N}_2$ ), magnesium nitride ( $\text{Mg}_3\text{N}_2$ ), boron nitride (BN), silicon nitride ( $\text{Si}_3\text{N}_4$ ), titanium nitride (TiN), vanadium nitride (VN), and copper(I) nitride were fluorinated with elementary fluorine.

When it became apparent that the action of fluorine upon the nitrides in general yields only small quantities of nitrogen trifluoride, ammonium fluoride and hydrazinium difluoride were added to the list of reactants.

### Experimental

Lithium, magnesium, and copper(I) nitrides and ammonium and hydrazinium fluorides were prepared by known methods. The other nitrides,  $\text{Be}_3\text{N}_2$ , BN,  $\text{Si}_3\text{N}_4$ , TiN, and VN were obtained from commercial sources. The fluorine employed in these studies was the commercially available compressed gas.

The fluorinations were carried out in a general-purpose type reactor made largely of monel metal and resembling that described by Priest.<sup>7</sup> The solid to be fluorinated was placed in a nickel boat or reactor tray made from a section of 0.5-in. nickel pipe, split lengthwise.

A monel tube, containing a tray of soda lime, which had been preheated in an oven at  $110$ – $120^\circ$  for several hours, followed the reactor. The purpose of this material was to react with any free fluorine which had passed through the reactor. The development of heat in this tube indicated when the reaction with the nitride was complete. A Dry Ice trap, a tube filled with sodium fluoride, and sodium hydroxide bubblers were introduced when necessary to remove hydrogen fluoride, silicon tetrafluoride, and

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boron trifluoride. The line was connected through a House-keeper 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<sub>3</sub> and N<sub>2</sub>O) 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.<sup>-1</sup>. The results are listed in Table I.

TABLE I  
NITROGEN TRIFLUORIDE CONTENT OF PRODUCT GASES

Substance fluorinated	% NF <sub>3</sub>	Substance fluorinated	% NF <sub>3</sub>	Substance fluorinated	% NF <sub>3</sub>
Li <sub>3</sub> N	0.01	BN	0.01	Cu <sub>3</sub> N	0.01
Li <sub>3</sub> N	0.1	Si <sub>3</sub> N <sub>4</sub>	0.03	NH <sub>4</sub> F	0.6
Bi <sub>3</sub> N <sub>2</sub>	0.2	Si <sub>3</sub> N <sub>4</sub>	0.3	NH <sub>4</sub> F	0.01
Mg <sub>3</sub> N <sub>2</sub>	0.06	TiN	0.00	N <sub>2</sub> H <sub>4</sub> F <sub>2</sub>	0.03
		VN	0.00	N <sub>2</sub> H <sub>4</sub> F <sub>2</sub>	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<sup>I</sup><sub>2</sub>TiCl<sub>6</sub> Compounds in Fused Antimony(III) Chloride

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The preparation of compounds of the type M<sup>I</sup><sub>2</sub>TiCl<sub>6</sub> (M<sup>I</sup> = K, Rb, Cs, NH<sub>4</sub>) has been described in the literature.<sup>1-9</sup> These salts can be obtained by precipitation from aqueous hydrochloric acid-titanium

tetrachloride solutions on addition of the corresponding alkali chloride,<sup>1-6</sup> by reaction of the solid alkali metal chloride with gaseous TiCl<sub>4</sub> at elevated temperatures (410°),<sup>7-8</sup> or, in some cases, by the reaction of TiCl<sub>4</sub> with the molten alkali metal chlorides.<sup>9</sup> 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.)<sup>10</sup> 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<sub>4</sub> 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,<sup>11</sup> and also TiCl<sub>4</sub> shows a good solubility in antimony trichloride melt. Hexachlorotitanates (e.g., K, Rb, Tl) are insoluble in the melt. After reaction, the solidified SbCl<sub>3</sub> 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 (≈1 g.) was dissolved in approximately 30 g. of double-distilled SbCl<sub>3</sub> in a Pyrex tube. After solidification of this mixture, TiCl<sub>4</sub> was added (10% more than required for the stoichiometric reaction 2MCl + TiCl<sub>4</sub>). The TiCl<sub>4</sub> 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<sub>4</sub> and the solvent SbCl<sub>3</sub> were extracted with distilled dry CS<sub>2</sub>. The remaining salt was dried from CS<sub>2</sub> 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 camera with Cu K<sub>α</sub> radiation.

## Results and Discussion

The salts K<sub>2</sub>TiCl<sub>6</sub> and Tl<sub>2</sub>TiCl<sub>6</sub> were prepared by using fused SbCl<sub>3</sub> 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<sub>2</sub>TiCl<sub>6</sub>: K, 23.08; Ti, 14.14; Cl, 62.78. Found: K, 23.1; Ti, 14.2; Cl,

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