TABLE I

COMPARISON OF RELATIVE AMOUNTS OF SILANES FROM Mg_2Si AND SiO

Silane yield ratio	SiO	Mg_2Si
Si_3H_8:n-Si_4H_{10}	2.3	2.8
n-Si_4H_{10}:n-Si_5H_{12}	2.2	3.0
n-Si_4H_{10}:i-Si_4H_{10}	8.0	13.8
n-Si_5H_{12}:i-Si_5H_{12}	2.5	2.8

the mean ratios of amounts of the silane isomers and homologs from magnesium silicide and from silicon monoxide (the ratios for magnesium silicide are little affected by the conditions under which it is prepared).

The total amount of silanes formed was determined by direct weighing of the volatiles. The theoretical yield was calculated by summing equations of the type

$$4SiO + 2H_2O = SiH_4 + 3SiO_2$$

$$(\text{or } 4SiO + 12HF = SiH_4 + 3SiF_4 + 4H_2O)$$

$$7SiO + 3H_2O = Si_2H_6 + 5SiO_2 \text{ etc.}$$

Knowing the relative yields of the different hydrides it was calculated that 160 g. of SiO (3.6 moles) should give 32 g. of mixed silanes (mean $SiH_{3.7}$). The experimental yields were variable, ranging from 9 to 24% of this theoretical yield. The cause of variability is uncertain but silicon monoxide samples giving high yields were found to be strongly adherent to the cold finger, *i.e.*, in good thermal contact with it.

The silicon monoxide was analyzed by reaction with alkali, by measuring the total gas evolution on dissolution in HF, and by the amount of silver formed on dissolving it in a solution of silver perchlorate in 20% HF.[5] The results all indicated an SiO content of 65–75%, *i.e.*, an Si : O ratio of 1 : 1.27 to 1 : 1.20 assuming that the rest is silica. It is not known if the apparent low purity was intrinsic or due to oxidative degradation before analysis as oxidation seemed rapid even with traces of oxygen present. However, it was found that the so-called Si_2O_3 made by Dadape and Margrave[6] also gave silanes with HF (the yield was 25–30% of theoretical, and the proportions of the different silanes were the same as from SiO), and it seems possible that if this species was present in the silicon monoxide it could account for the apparent high oxygen content and in part for silane evolution. The silicon monoxide samples contained 0.1–0.5% of HF involatile impurities. Analysis of these indicated that aluminum was the main metallic impurity in the monoxide; the magnesium content of the monoxide was below 0.02%.

Germanium monoxide prepared in a similar way from germania and germanium is almost insoluble in 10% HF. However, it was found that by condensing silicon monoxide and germanium monoxide together on the cold finger a black solid with a green sheen was obtained which gave silanes, silicon–germanium hydrides,[7,8] and germanes with 10% HF. A maximum of about 15% of the total volatiles were silicon–germanium hydrides (as $SiGeH_6$, Si_2GeH_8, Si_3GeH_{10}, Si_4GeH_{12}, with smaller amounts of $Si_2Ge_2H_{10}$ and $SiGe_2H_8$) with about 1% of germanes (as GeH_4, Ge_2H_6, and Ge_3H_8). If the germanium content of the solid was more than about 20% it was almost insoluble in the acid and gave only traces of hydrides.

Boron monoxide was also prepared in the same furnace system from boric oxide and boron.[9] The light brown condensates formed frequently exploded when scratched in air. They dissolved in water to give a solution which in 2 hr. evolved 0.3% of the boron as volatile boranes, and these were shown gas chromatographically to be mainly tetra- and pentaborane in a 5:1 mole ratio.

When hydrogen was passed over a mixture of silicon and silica at 1200° some monosilane was formed as has already been reported,[10] but the yields were tiny even with efficient quenching of the gases. A fibrous form of silica was deposited where the gas was quenched. Rapid cooling of the gases after passing hydrogen over heated boron and boric oxide[11] gave some diborane and also a white solid, probably boroxine $(HBO)_3$,[12] which evolved diborane together with tetra- and pentaborane on heating to 150°.

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Group VA and Group VIIA Oxofluorosulfates

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Some transition metal oxofluorosulfates have been prepared, *e.g.*, $MoO_2(SO_3F)_2$[1] and $CrO_2(SO_3F)_2$,[2] but no attempt has been made toward a systematic preparation and characterization of others of these transition metal compounds. A rewarding route is provided by the use of a transition metal or its anhydrous chloride in reaction with peroxodisulfuryl difluoride ($S_2O_6F_2$).

Experimental

Materials.—Peroxodisulfuryl difluoride was prepared by the catalytic fluorination of sulfur trioxide.[3] Niobium and rhenium metals were 99.9% pure. Anhydrous metal chlorides used were at least 99% pure. All other materials were of analytical reagent grade.

Analytical Methods.—Elemental analyses were obtained after basic hydrolysis in dilute sodium hydroxide. Sulfate was pre-

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cipitated as barium sulfate; fluorine was determined using a null-point method[4,5]; and oxygen was obtained by difference.

All reactions studied were carried out in Pyrex vessels similar to that described for the preparation of $MoO_2(SO_3F)_2$.[1] However, since it had been observed previously that $S_2O_6F_2$ dissolves Kel-F stopcock grease, a stopcock was not attached to the reaction vessel. $S_2O_6F_2$ was transferred from the storage container to a 12-mm. o.d. Pyrex tube which was connected to the reaction vessel through a glass line. Transfer of the reagent from the tube to the reaction vessel essentially precluded contamination of the product by stopcock grease. Since $S_2O_6F_2$ is readily hydrolyzed and the compounds prepared are highly hygroscopic, all reactions were run under high vacuum conditions.

Oxotris(fluorosulfato)vanadium(V).—Approximately 0.03 mole of vanadyl(V) chloride, which is a yellow, rather volatile liquid at room temperature and which may be transferred in a vacuum system with some ease, was allowed to react with an excess of $S_2O_6F_2$ by freezing the latter on top of the former at −195°. After the mixture was allowed to warm to room temperature, a vigorous, mildly exothermic, reaction ensued. The contents of the reaction vessel changed from yellow to green and finally to a yellow-brown solid material which completely covered the inner surface of the vessel. Large amounts of chlorine were released in the reaction and were transferred to another vessel while the reaction vessel was held at −40°. The vessel was sealed and heated at 60° for about 72 hr. A very nonvolatile, viscous, deep red liquid which was more dense than $S_2O_6F_2$ remained when the excess of the latter was removed. A bright yellow-orange liquid, identified as chlorine fluorosulfate,[6] also distilled from the flask. The viscous, deep red liquid reacted very vigorously with 0.1 *N* sodium hydroxide solution according to the equation

$$VO(SO_3F)_3 + 12OH^- = 3SO_4^{2-} + 3F^- + VO_4^{3-} + 6H_2O$$

when the solution was heated at 100° for 24 hr. After hydrolysis was complete, the alkaline solution was colorless. However, since upon acidification with nitric acid the solution became yellow, the presence of a vanadium(V)-containing species was indicated. Vanadium was determined by oxidation with standard potassium permanganate after reduction to vanadium(IV) with sulfur dioxide. Sulfur and fluorine were determined as described above. No chlorine was found in the solution. The ratio, in terms of atoms, found for V:S:F was 1.0:2.9:2.9 compared to 1:3:3 theoretical for $VO(SO_3F)_3$.

Anal. Calcd. for $VO(SO_3F)_3$: V, 14.0; S, 26.1; F, 15.7. Found: V, 14.0; S, 25.4; F, 15.1.

The compound is a viscous deep red liquid which fumes in moist air, is highly hygroscopic, and is stable at temperatures in excess of 200°.

Oxotris(fluorosulfato)niobium(V).—A 1.8-mmole sample of niobium(V) chloride was introduced into a reaction bulb and an excess of $S_2O_6F_2$ was allowed to condense onto the solid. Little or no reaction was observed at room temperature. The flask was sealed and placed in an oven at about 60°. As the reaction proceeded, the yellow crystalline $NbCl_5$ changed first to a white solid and then finally became a viscous yellow liquid that was insoluble in, and more dense than, the excess $S_2O_6F_2$. After 100 hr., no further reaction was observed and the excess $S_2O_6F_2$ was removed. Chlorine fluorosulfate and pyrosulfuryl fluoride were identified as volatile products. No free chlorine was found.

The yellow liquid hydrolyzed readily in 0.1 *N* sodium hydroxide according to the reaction

$$2NbO(SO_3F)_3 + 18OH^- = \underline{Nb_2O_{5hyd}} + 6SO_4^{2-} + 6F^- + 9H_2O$$

The basic solution was filtered and the precipitate, hydrous Nb_2O_5, was washed, ignited, and weighed as Nb_2O_5. No chlorine was found in the solution. Sulfur and fluorine were determined as above. The experimental mole ratio Nb:S:F was 1.0:3.0:4.1 compared to 1:3:3 calculated for $NbO(SO_3F)_3$.

Anal. Calcd. for $NbO(SO_3F)_3$: Nb, 22.9; S, 23.6; F, 14.0. Found: Nb, 21.9; S, 22.5; F, 18.2. It was found that as little as 2 × 10^{-4} g. of niobium in 50 ml. of solution caused extremely high fluorine results to be obtained.

Powdered niobium metal was used initially in reaction with $S_2O_6F_2$ to prepare $NbO(SO_3F)_3$. However, since it was difficult to obtain complete reaction, due to the formation of a protective coating on the metal surface by the reaction product, the metal was discarded as a source of niobium.

The compound is a viscous, yellow liquid which fumes in moist air and is highly hygroscopic.

Oxotris(fluorosulfato)tantalum(V).—An analogous reaction with tantalum(V) chloride also produced a viscous yellow liquid which hydrolyzed readily in dilute sodium hydroxide to give a precipitate of white, hydrous Ta_2O_5. Chlorine fluorosulfate and pyrosulfuryl fluoride were volatile products formed in the initial reaction between $TaCl_5$ and $S_2O_6F_2$. Complete precipitation of tantalum was ensured by the addition of ammonium oxalate and tannin. This precipitate was ignited and weighed as Ta_2O_5. The experimental ratio Ta:S was 1.0:3.2 compared to 1:3 calculated for $TaO(SO_3F)_3$.

Anal. Calcd. for $TaO(SO_3F)_3$: Ta, 36.6; S, 19.5. Found: Ta, 35.9; S, 20.1.

The compound is a dense, viscous yellow liquid, is highly hygroscopic, and is thermally stable at temperatures up to at least 300°. The compound becomes red at these temperatures and returns to its characteristic yellow color on cooling.

Dioxotris(fluorosulfato)rhenium(VII) and Trioxo(fluorosulfato)rhenium(VII).—Depending upon experimental conditions, one or two rhenium(VII)-containing compounds may be obtained. When a moderate excess of $S_2O_6F_2$ is caused to react with metallic rhenium, two phases, a white solid and a nonvolatile yellow liquid, are found in the bulb, in addition to the remaining unreacted $S_2O_6F_2$ and $S_2O_5F_2$ which can be distilled away. If a large excess of $S_2O_6F_2$ is used, it is possible to obtain only the yellow liquid. Upon heating, the white solid is converted irreversibly to the yellow liquid. These reactions can best be shown by the unbalanced equations

$$Re + S_2O_6F_2 \longrightarrow \underset{\text{yellow liq.}}{ReO_3(SO_3F)} + \underset{\text{white solid}}{ReO_2(SO_3F)_3} + S_2O_5F_2$$

$$Re + S_2O_6F_2\ (\text{excess}) \xrightarrow{\Delta} \underset{\text{yellow liq.}}{ReO_3(SO_3F)} + S_2O_5F_2$$

$$ReO_2(SO_3F)_3 \xrightarrow{\Delta} ReO_3(SO_3F) + S_2O_5F_2$$

Since separation of the two compounds is difficult, it is likely that the solid was contaminated with small amounts of the yellow liquid. After the solid material was pumped on until a constant weight loss per unit time was observed and was hydrolyzed in dilute sodium hydroxide at 100° for 48 hr., elemental analyses were run. Rhenium was determined using nitron, fluorine as lead chlorofluoride after distillation, and sulfur as above. The molar ratio Re:S:F is 1.0:2.8:3.2 compared to 1:3:3 for $ReO_2(SO_3F)_3$.

Anal. Calcd. for $ReO_2(SO_3F)_3$: Re, 36.1; S, 18.6; F, 11.1. Found: Re, 37.1; S, 17.9; F, 12.1.

The compound is a hygroscopic, white solid which is readily converted to a yellow liquid and pyrosulfuryl fluoride on heating.

After 36 hr., a 0.5-g. sample of finely powdered rhenium metal had completely reacted with a large excess (5 ml.) of $S_2O_6F_2$ to give a very viscous yellow oil which appeared to be soluble in the excess $S_2O_6F_2$. The unreacted $S_2O_6F_2$ and $S_2O_5F_2$ were transferred under high vacuum conditions to another container and the yellow liquid was maintained at 80° for several hours until no volatile material was observed in a trap between the reaction vessel and the vacuum pump. After hydrolysis at 100°, rhenium and sulfur were determined as above and fluorine through the use of the null-point method. The mole ratio Re:S:F was 1.0:1.1:1.1 compared to 1:1:1 calculated for $ReO_3(SO_3F)$.

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[4] T. A. O'Donnell and D. F. Stewart, *Anal. Chem.*, **33**, 337 (1961).

[5] T. A. O'Donnell and D. F. Stewart, *ibid.*, **34**, 1347 (1962).

[6] W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2**, 496 (1963).

Anal. Calcd. for $ReO_3(SO_3F)$: Re, 55.9; S, 9.6; F, 5.7. Found: Re, 55.5; S, 10.3; F, 6.2.

The compound is a very viscous, highly hygroscopic, yellow liquid with a melting point of approximately −33°. (A freezing point was not obtained since the liquid tended to supercool and solidified to a glass.)

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The Preparation of Trisdimethylaminostibine

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Dialkylamino derivatives of triply-connected phosphorus[1] and arsenic[2] have been prepared in good yields by the aminolysis of the corresponding trihalides.

$$MX_3 + 6NHR_2 \longrightarrow M(NR_2)_3 + 3NHR_2 \cdot HX \quad (1)$$

(M = P, As; X = halogen; R = alkyl). Preliminary experiments showed that antimony trichloride, when allowed to react with dimethylamine according to eq. 1, formed ill-defined addition products with the amine. At room temperature, a complex of the composition $SbCl_3 \cdot 4NH(CH_3)_2$ appeared to be stable. At 100° *in vacuo*, the complex lost one mole of dimethylamine to give $SbCl_3 \cdot 3HN(CH_3)_2$, but it did not sublime.

Recently it has been reported that dialkylamino compounds of transition metals[3,4] are readily obtained by treating the metal halide with lithium dialkylamides. We have applied this method to the preparation of trisdimethylaminostibine from antimony trichloride and lithium dimethylamide

$$SbCl_3 + 3LiN(CH_3)_2 \longrightarrow Sb[N(CH_3)_2]_3 + 3LiCl \quad (2)$$

The trisdimethylaminostibine was obtained in 62% yield. The compound is a colorless liquid which is extremely sensitive to moisture. Exposure to air causes the immediate formation of a white precipitate of Sb_2O_3 due to hydrolysis.

The proton n.m.r. spectrum of $Sb[N(CH_3)_2]_3$ exhibits one sharp resonance which is consistent with its structure. As shown in Table I, this resonance is downfield of that of the analogous arsenic compound which, in turn, is at a lower field than that of the corresponding phosphorus compound. For increasing electronegativity of the central atom, the methyl resonance appears at increasing values of the applied field. No definite trend has been observed for some tetrakisdimethylamino derivatives of group IV elements (Table I). This variation in resonance frequency with the electronegativity for dimethylamino compounds of group V elements is in marked contrast to that observed for methyl esters of inorganic acids.[5] In the latter case, it was found that the resonance for the methyl protons appears at decreasing values of the applied field as the electronegativity of the central atom increases. This is in agreement with the comfortable idea of increased deshielding of the methyl protons with increasing electronegativity of a heteroatom farther away in the molecule. The theory of the neighbor-anisotropy effect[6] indicates that the opposite behavior, shown in Table I for the group V compounds, is due to a change in the average angle between the nuclear axis of magnetic anisotropy of the atom M and the M–N bond in the moiety $M\text{–}NR_2$, when atom M is changed from P to As to Sb.

TABLE I

PROTON N.M.R. DATA OF SOME DIMETHYLAMINO DERIVATIVES OF GROUP IV AND V ELEMENTS

	δ, p.p.m.[a]	$J_{C^{13}-H}$, c.p.s.	Electronegativity of central atom
$P[N(CH_3)_2]_3$	−2.425[b]	132.5[c]	2.1[d]
$As[N(CH_3)_2]_3$	−2.533	131.8	2.0
$Sb[N(CH_3)_2]_3$	−2.700	131.5	1.9
$Si[N(CH_3)_2]_4$	−2.417	131.0	1.8
$Ge[N(CH_3)_2]_4$	−2.563	131.2	1.8
$Ti[N(CH_3)_2]_4$[e]	−3.033	132.5	1.5

[a] Measured as neat liquids relative to tetramethylsilane as internal standard. All signals shifted downfield by 0.03 p.p.m. upon dilution with 10 parts of benzene. [b] J_{P-H} = 8.7 c.p.s. [c] $J_{P-C^{13}-H}$ = *ca.* 8 c.p.s. [d] Electronegativities: L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 93. [e] Prepared by M. D. Rausch.

Experimental

Aminolysis of Antimony Trichloride.—A quantity of 9.7372 g. of dimethylamine was condensed on 2.8286 g. of antimony trichloride and sealed *in vacuo*. On warming to room temperature, a fairly vigorous reaction occurred forming a clear solution. After several days of standing at room temperature, the excess dimethylamine was distilled off, yielding a white solid residue analyzing as $SbCl_3 \cdot 4.089NH(CH_3)_2$. Heating of this residue at 100° *in vacuo* caused the distillation of additional dimethylamine, resulting in a residue of the composition $SbCl_3 \cdot 3.019NH(CH_3)_2$. Attempts to sublime this product *in vacuo* failed; the initially off-white material liquefied and turned black and no volatile products were observed.

Preparation of Trisdimethylaminostibine.—Special precautions, *e.g.*, carefully dried glass apparatus, were adopted to avoid hydrolysis. All procedures were performed under an atmosphere of dry oxygen-free nitrogen. Dried reagents were used.

To a cooled (Dry Ice–acetone) solution of 71.6 g. (1.1 moles) of *n*-butyllithium in 725 ml. of hexane was added a solution of 50.3 g. (1.1 moles) of dimethylamine in 500 ml. of diethyl ether and 350 ml. of hexane. The resulting suspension of lithium dimethylamide was then stirred at room temperature for 20 min. After cooling the flask again with Dry Ice–acetone, a solution of 85 g. (0.37 mole) of antimony trichloride in 150 ml. of diethyl ether was added over a period of 1 hr. Subsequently, the reaction mixture was refluxed for 1 hr., and, after removal of the solvents, the product distilled as a colorless liquid at 32–34° (0.45 mm.), yield 58 g. (62%).

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