trace of methanol added at this point immediately gave evidence of germanium(II) production.

Sodium hypophosphite in aqueous 3 *M* hydrochloric acid has also been found to be an effective reducing medium for germanium tetrachloride, presumably *via* reaction 1. It has thus been possible to precipitate out, for the first time, a $(Ge^{II}Cl_3)_2$ salt by adding ethylenediammonium chloride to the aqueous $GeCl_2$ species. White crystals of ethylenediammonium bis[trichlorogermanate(II)] appeared upon volume reduction and cooling.

Work is currently under way to generalize new reaction pathways for the facile isolation and preparation of all the GeX_2 salts (X = F, Cl, Br, I) and new divalent germanium species in methanolic hypophosphite. In addition, diverse inorganic and organic systems are currently being treated and tested with $NaH_2PO_2 \cdot H_2O$ in methanol. It has, for instance, recently been found that silver(I) and copper(II) salts are reduced to the elemental metallic state. Mercury(II) chloride is reduced halfway to the mercury(I) chloride salt, Hg_2Cl_2.

Experimental Section

Preparation of $(CH_3)_3NH^+[Ge(HPO_3)Cl]^-$. Sodium hypophosphite monohydrate (J. T. Baker Chemical Co.) was dried at 110° for 1 hr with no significant weight loss. In a typical experiment, 18.4 g (0.086 mmol) of germanium tetrachloride (Eagle-Picher Chemical Co.) in 75 ml of absolute methanol was cooled to 0° and then added to 9.1 g (0.086 mol) of $NaH_2PO_2 \cdot H_2O$ in 100 ml of the same solvent also at 0°. The reductive reaction was essentially over upon mixing of solutions. A white precipitate (4.5 g, 0.077 mol, 90% yield) of NaCl formed during the above mixing process and was filtered off. Addition of trimethylammonium chloride (0.086 mol) to the filtrate immediately precipitated out another white salt (13.42 g, 63% yield) formulated as $(CH_3)_3NH^+[Ge(HPO_3)Cl]^-$. *Anal.* Calcd for $C_3H_{11}NO_3PClGe$: C, 14.52; H, 4.44; N, 5.64. Found: C, 14.63; H, 4.39; N, 5.61. Analyses were performed by M-H-W Laboratories, Garden City, Mich.

The above reaction took place either under atmospheres of nitrogen or ordinary air. Reduction was also observed in solvents *n*-hexanol and formic acid, but reaction times were lengthened to several hours and yields of germanium(II) species were invariably lowered.

Preparation of $Ge(HPO_3)$ or $Ge(HPO_3) \cdot H_2O$. In like manner to the above, germanium tetrachloride was reduced with methanolic sodium hypophosphite, the solid sodium chloride filtered off, and the volume of filtrate solution slowly reduced (under vacuum) until white crystals first appeared. A 72% yield of solid formulated as $Ge(HPO_3) \cdot H_2O$ was obtained. *Anal.* Calcd for H_3O_4PGe: P, 18.16. Found: P, 17.85.

Infrared data (cm^{-1}, Nujol mulls and KBr pellets): 3300 m, br (O–H stretch); 2475 w (P–H stretch); 1650 m, br (O–H bend); 1187 s (P=O stretch); 1055 vs, br (P–O stretch); 848 s and 600 m, br (Ge^{II}–O stretch).

Nmr spectra were recorded in pure methanol or deuterated methanol (Stohler Isotope Chemicals) on a Varian Associates T-60 instrument.

The white crystals melt with decomposition at about 255° (lit.[3] mp 230°). They are readily hydrolyzed, producing the characteristic yellow, yellow-orange color of hydrated germanium(II) hydroxide.

Preparation of $(H_3N^+CH_2CH_2NH_3^+)(GeCl_3^-)_2$. Ethylenediammonium bis[trichlorogermanate(II)] was prepared by mixing equimolar quantities of $GeCl_4$ and $NaH_2PO_2 \cdot H_2O$ in 3 *M* HCl, adding ethylenediammonium chloride, removing solvent under vacuum until white solid first appeared, and then cooling to grow crystals. A 48% yield was thus obtained. *Anal.* Calcd for $C_2H_{10}N_2Cl_6Ge_2$: C, 5.72; H, 2.38; N, 6.66. Found: C, 5.79; H, 2.32; N, 6.89. Analysis was performed by the Analytical Services Division of Northwestern University. The salt is high melting (>300° dec) and is readily hydrolyzed to germanium(II) hydroxide species.

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Registry No. $(CH_3)_3NH^+[Ge(HPO_3)Cl]^-$, 42579-16-8; $Ge(HPO_3)$, 29850-62-2; $(H_3N^+CH_2CH_2NH_3^+)(GeCl_3^-)_2$, 42579-17-9; $NaH_2PO_2 \cdot H_2O$, 10039-56-2; $GeCl_4$, 10038-98-9.

Contribution from Departamento de Quimica Organica, Facultad de Ciencias Exactas and Instituto de Investigaciones Fisicoquimicas Teoricas y Aplicadas, La Plata, Argentina

Preparation of Two New Haloalkyl Fluorosulfates: Dichloromethyl Fluorosulfate ($CHCl_2OSO_2F$) and 1,1,2-Trichlorofluoroethyl Fluorosulfate ($CHClFCCl_2OSO_2F$)

L. F. R. Cafferata* and J. E. Sicre

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Studies have been made of the reactivity of several fluoroxy compounds such as fluoroxytrifluoromethane[1] (CF_3OF), 2-fluoroxyperfluoropropane ($(CF_3)_2CFOF$), 2-fluoroxy-2-trifluoromethylperfluoropropane ($(CF_3)_3COF$), and bis(fluoroxy)difluoromethane ($CF_2(OF)_2$) as electrophilic fluorinating agents of organic substrates.[2]

Williamson, *et al.*,[3-5] reported the addition of fluoroxysulfur pentafluoride (SF_5OF) to various simple halogenated olefins. Fluorine fluorosulfate (FSO_2OF) also adds to fully halogenated alkenes.[6,7]

In this work we study, under controlled conditions, the reactivity of fluorine fluorosulfate on hydrogenated haloalkanes and -alkenes, such as chloroform and trichloroethylene.

We report a simple and efficient method to obtain the following two new compounds: dichloromethyl fluorosulfate (I) and 1,1,2-trichlorofluoroethyl fluorosulfate (II). The method is based upon the reactions

$$CHCl_3 + F_2SO_3 \xrightarrow{-78^\circ} \underset{\mathrm{I}}{CHCl_2OSO_2F} + ClF \qquad (1)$$

$$CHCl{=}CCl_2 + F_2SO_3 \xrightarrow{-78^\circ} \underset{\mathrm{II}}{CHClFCCl_2OSO_2F} \qquad (2)$$

Chlorine monofluoride was not detected as a product of reaction 1. Instead, a heavy attack at the glass reactor exit was observed. A small amount of trichlorofluoromethane was obtained as a by-product. So far, we cannot conclude whether the trichlorofluoromethane formed came as a result of the direct fluorination of chloroform either by fluorine fluorosulfate or by chlorine monofluoride. Nevertheless, (1) represents a new type of reaction for fluorine fluorosulfate.

Experimental Section

Materials. Chemicals were reagent grade. Chloroform was freed from ethanol by repeated washing with water, dried over potassium carbonate, and finally distilled. Pure fluorine fluorosulfate obtained photochemically was employed.[8]

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General Procedure. The reactions were carried out in an all-Pyrex-glass reactor, with stopcocks and joints lubricated with "Halocarbon" grease. A stream of dry nitrogen (2 l/hr) saturated with fluorine fluorosulfate at −78° (~50 mm) was bubbled into the haloalkane (or haloalkene) cooled also at −78°.

When all the fluorine fluorosulfate had reacted and the inert gas was pumped out of the reactor at −190°, the liquid was warmed up to room temperature. Then it was treated with a saturated solution of sodium bicarbonate and repeatedly washed with distilled water. Finally it was dried over anhydrous potassium carbonate. The components of the liquid mixture were determined by vpc chromatography in an F & M model 810 instrument equipped with a thermal conductivity detector and an analytical column (1.65 mm × 1.8 m) packed with Chromosorb W (AW-TMCS) impregnated with 10% Carbowax 20 M.

The reaction products could be separated with a preparative column (12.5 mm × 2.40 m) packed with Chromosorb W (AW-TMCS) impregnated with 10% silicone gum rubber SE-30.

The infrared spectra of the products were obtained on a Perkin-Elmer Model 337 spectrophotometer using cells equipped with KBr windows. Nuclear magnetic resonance spectra were recorded on a DP-60 Varian Associates instrument. Trichlorofluoromethane and tetramethylsilane were used as internal standards. The vapor pressures of the products were measured with a mercury manometer, using a quartz spiral as a null instrument.

Molecular weights were determined by the gas chromatographic method.[9] Elemental analyses were carried out making use of microchemical techniques.[10]

Preparation of Dichloromethyl Fluorosulfate (I). The reaction of 0.06 mol of fluorine fluorosulfate and 0.5 mol of chloroform yielded 80% product I and 13% trichlorofluoromethane.

The reaction is rapid and exothermic. Compound I is a colorless liquid which slowly decomposes at room temperature; mp −66.0 ± 0.5°. The vapor pressure is given by $\log p(\text{mm}) = 8.00 - 1890/T(^\circ\text{K})$ (between 2 and 20°) and $\Delta H_{\text{vap}} = 8.6$ kcal mol^{-1}. The Trouton constant is 23.4 eu; bp (extrapolated) 95.8°. *Anal.* Calcd for CHO_3Cl_2FS: C, 6.56; H, 0.55; Cl, 38.75; F, 10.38; S, 17.52. Found: C, 6.45; H, 0.44; Cl, 38.89; F, 10.13; S, 17.62. The molecular weight was found to be 188 (theoretical 183.0).

The ^{19}F nmr spectrum shows δ_{SF} −44.4 ppm (*e.g.*, in perfluoroethyl fluorosulfate,[6] δ_{SF} is −49.4 ppm). The ^1H nmr spectrum indicates δ_{CH} +7.50 ppm (*e.g.*, in chloroform, δ_{CH} is +7.24 ppm).

The assignment of some infrared bands of I is as follows (ν in cm^{-1}): 3010 (m) (C–H); 1438 (m) (S–O asymmetric stretch), 1228 (s) (S–O symmetric stretch), 859 (s) (S–F). Other bands not identified are 944 (s), 2670 (vw), 1720 (w), 1305 (m), 1105 (m), 803 (m), 747 (w), 720 (w), 570 (m), 540 (w), 528 (w), and 430 (w) cm^{-1}.

Preparation of 1,1,2-Trichlorofluoroethyl Fluorosulfate (II). The reaction of 0.1 mol of fluorine fluorosulfate and 0.2 mol of trichloroethylene yielded 70% product II and 4% trichlorofluoroethylene. This is also a rapid and exothermic reaction. Compound II is a colorless liquid which is stable at room temperature. A sample (0.2 ml) sealed in a Pyrex ampoule and heated for 2 hr at 110° partially decomposes into trichlorofluoroethylene and fluorosulfuric acid: $CHClFCCl_2OSO_2F \rightarrow CClF{=}CCl_2 + FSO_2OH$. The pyrolysis products were identified by their infrared spectra. The melting point of II was not measured with the accuracy reported for I. On cooling this compound to −196° a cracked solid was formed. The temperature at which the cracked appearance vanished is about −20°. The vapor pressure is given by $\log p(\text{mm}) = 7.43 - 1911/T(^\circ\text{K})$ (between 44 and 80°) and ΔH_{vap} 8.7 kcal mol^{-1}. The Trouton constant is 20.8 eu; bp (extrapolated) 146.8°. The density at 20° is 1.632 g cm^{-3}; n^{20}D 1.4162. *Anal.* Calcd for $C_2HO_3Cl_3F_2S$: C, 9.62; H, 0.40; Cl, 42.66; F, 15.24; S, 12.83. Found: C, 9.79; H, 0.47; Cl, 42.77; F, 15.03; S, 12.98. The molecular weight was found to be 247 (theoretical 249.4).

The ^{19}F nmr spectrum of II shows δ_{SF} −50.78 ppm and a doublet centered at +139.07 ppm ($J_{FH} = 47.92$ Hz). The ^1H nmr spectrum of II shows a doublet centered at +6.31 ppm ($J_{FH} = 48.20$ Hz). Comparison of this value with the spectrum of $CHClFCHClOSF_5$[5] confirms the structure of product II.

The assignment of some infrared bands of II is as follows (ν in cm^{-1}): 2940 (m) (C–H), 1400 (s) (S–O asymmetric stretch), 1235 (s) (S–O symmetric stretch), 1075 (s) (C–F stretch), 890 (s) (S–F). Other bands not identified are 1253 (m), 1112 (m), 1060 (w), 1055 (w), 975 (w), 950 (s), 865 (s), 845 (m), 820 (w), 810 (s), 785 (m), 670 (w), 650 (m), 598 (w), 570 (m), 550 (m), 535 (m), and 500 (m) cm^{-1}.

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Registry No. $CHCl_2OSO_2F$, 42016-50-2; $CHClFCCl_2OSO_2F$, 42087-88-7; $CHCl_3$, 67-66-3; F_2SO_3, 13536-85-1; $CHCl{=}CCl_2$, 79-01-6.

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[10] Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach uber Engelskirchen, West Germany.

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada

Convenient Synthesis of Hexaammineosmium(III)

Frank Bottomley* and Shiu-Bor Tong

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Hexaammineosmium(III), $[Os(NH_3)_6]X_3$ (X = Br, I, and ($OsBr_6$/3), was synthesized previously (32% yield) by reaction of $(NH_4)_2OsBr_6$ with ammonia in a sealed tube for 1 month.[1-4] This time-consuming procedure appears to be responsible for the lack of information on this complex[1-5] compared to its ruthenium analog.[6-12] During investigation of reactions of $[Os(NH_3)_5NO]^{3+}$ we found reduction with zinc in ammonia gave $[Os(NH_3)_6]^{3+}$.[13] This suggested Zn–NH_3 reduction of commercial $(NH_4)_2OsCl_6$ would give $[Os(NH_3)_6]^{3+}$ also. Such was the case, and the preparation and some properties of $[Os(NH_3)_6]X_3$ (X = Cl, Br, I, and ClO_4) are reported.

Results and Discussion

Reduction of $(NH_4)_2OsCl_6$ with zinc dust in 0.880 g cm^{-3} of ammonia for 5 hr gave a pale yellow solution and metallic osmium. Addition of potassium iodide to the solution gave $[Os(NH_3)_6]I_3$ (32%), from which other salts were obtained metathetically. Increasing the reduction time increased the amount of metallic osmium, and with shorter times the product was contaminated with osmium(IV). $[Os(NH_3)_6]^{2+}$ was not observed, in contrast to ruthenium chemistry, where $[Ru(NH_3)_6]^{2+}$ was obtained by a similar reaction.[14]

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