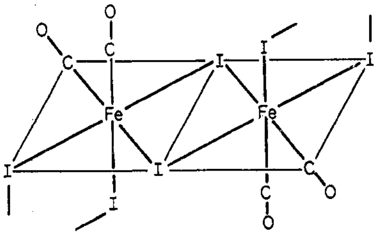


Figure 3.—The structure proposed for $[Fe(CO)_2I_2]_n$.

tained: 27°, 11.4 ml, 35 torr, weight of sample 6.6 mg. From these data a molecular weight of 305 ± 10 was obtained. Other similar measurements gave values of 290, 270, and 300, all ±10. The average, 290, may be compared with the theoretical value of 295 for $Fe(CO)_4I$. The approximate equilibrium vapor pressure over the liquid at 25° is 45 torr.

The diamagnetism of the compound in xylene solution at 25° was demonstrated by the nmr method of Evans.[11]

Preparation of $Fe(CO)_2I_2$.—$Fe_2(CO)_8I_2$ in tetrahydrofuran was treated with 2 equiv of iodine in the same solvent. After shaking for 1 hr the solvent was removed under vacuum. A dark brown powder was obtained. This product was insoluble in a wide range of solvents and decomposed instantaneously on contact with air.

$Fe(CO)_2I_2$ was also obtained by the method of Hieber and Legally.[9]

(11) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

Contribution from Rohm and Haas Company,
Redstone Research Laboratories,
Huntsville, Alabama 35807

Studies Involving Some Nonmetal Oxy- and Thiofluoride Salts

By Max Lustig and John K. Ruff

Received June 8, 1967

Some recent publications describe the reactions of carbonyl fluoride, perfluoroalkylacyl fluorides, and ketones with alkali metal fluorides.[1-3] It was of interest to extend this study to other compounds. For example, in the case of thionyl tetrafluoride, SF_4O, the reaction with cesium fluoride led to the formation of the complex pentafluorosulfoxide anion, SF_5O^-. This ion has been considered to be an intermediate when thionyl fluoride, SF_2O, or SF_4O is fluorinated in the presence of cesium fluoride to form pentafluorosulfur hypofluoride, SF_5OF,[4] but the intermediate has always been prepared *in situ* and no details have been reported regarding its preparation or properties. No attempt was made to isolate the pure $CsOSF_5$ salt because it slowly decomposes to SF_4O and cesium fluoride, and only a partial characterization of the complex salt is presented below.

When phosphoryl fluoride, PF_3O, was used as a substrate toward cesium fluoride, there was no evidence for the formation of the PF_4O^- ion. Instead, an oxygen for fluorine-exchange reaction occurred and equimolar quantities of two products—cesium difluorodioxophosphate, $CsPO_2F_2$,[5] and cesium hexafluorophosphate, $CsPF_6$—were formed according to the equation

$$2CsF + 2PF_3O \longrightarrow CsPF_2O_2 + CsPF_6$$

The corresponding thio derivative, PF_3S, behaved in a similar manner toward attack by cesium fluoride and quantitatively produced the new difluorodithiophosphate ion,[6] $PF_2S_2^-$, as well as the PF_6^- ion. This same reaction now has also been found to take place nearly quantitatively when potassium fluoride is employed. Similarly, reaction between thiophosphoryl chloride, $PSCl_3$, and potassium fluoride also yields the fluorophosphates, KPS_2F_2 and KPF_6, by the route

$$8KF + 2PSCl_3 \longrightarrow KPF_2S_2 + KPF_6 + 8KCl$$

The alkali metal difluorodithiophosphate salts have been converted to the corresponding tetraphenylarsonium and bis(triphenylphosphine)immonium derivatives. The infrared and ^{19}F nmr spectra of the pentafluorosulfoxide and the difluorodithiophosphate ions have been examined.

Experimental Section

Reagents.—Thiophosphoryl trichloride and the potassium and cesium fluorides were procured from Alfa Inorganics, Inc. The alkali metal fluorides were heated to 300° while pumping and then ground to fine powders before using. The trichloride was converted to the trifluoride by the method of Tullock and Coffman[7] and it was purified by gas partition chromatography using a 15-ft perfluorotri-*t*-butylamine on Chromosorb P column at −30°. All solvents were dried by storage over 5A molecular sieves.

Apparatus and General Procedure.—A standard Pyrex vacuum apparatus was used for transfer and purification of gaseous materials. All chemicals were handled with the strict exclusion of moisture. The reactors were 50-ml thick-walled Pyrex bulbs with Fisher-Porter Teflon valves unless otherwise stated. Infrared spectra of the solids were taken as Nujol mulls using a Perkin-Elmer 521 spectrometer in the 4000–200-cm^{-1} region. Cesium bromide plates were employed. Salts containing the known $PO_2F_2^-$ and PF_6^- ions were identified by the infrared bands near 1140 and 1310 cm^{-1} in the spectra of the former and near 840 cm^{-1} [8] in those containing the latter. The ^{19}F nmr spectra were obtained with a Varian Model V4310 spectrometer operating at 40 Mc using dimethyl sulfoxide, DMSO, as a solvent for the samples and fluorotrichloromethane as an internal standard. Samples were placed in 5-mm o.d. Pyrex tubes.

Reaction between CsF and PF_3O. A. Neat.—Cesium fluoride, 0.817 g (5.36 mmoles), was charged into the reactor. While holding the vessel at −196°, PF_3O (5.50 mmoles) was added. The bulb was then heated to 100° for 1 hr. A small pressure decrease was observed, and then the temperature of the reactor was raised to 135° for a 24-hr interval. A small amount of PF_3O remained in the gas phase. After pumping to constant weight the increase in weight of the solid phase corresponded to the absorption of 5.35 mmoles of PF_3O or 99.5% yield based on a 1:1 PF_3O to CsF mole ratio. The $PF_2O_2^-$ and PF_6^- ions were identified by comparing their infrared and nmr spectra with the

---

(1) D. C. Bradley, M. E. Redwood, and C. J. Willis, *Proc. Chem. Soc.*, 416 (1965).

(2) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

(3) M. Lustig, A. R. Pitochelli, and J. K. Ruff, *J. Am. Chem. Soc.*, **89**, 2841 (1967).

(4) J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

(5) W. Lange, *Ber.*, **62B**, 786 (1929).

(6) H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *J. Am. Chem. Soc.*, **89**, 1272 (1967).

(7) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

(8) K. Bühler and W. Bues, *Z. Anorg. Allgem. Chem.*, **308**, 65 (1961).

known spectra. Also, the ^{19}F spectrum of the sample of the product mixture indicated that both ions were present in equal amounts.

B. CH_3CN Slurry.—Onto 0.398 g (2.62 mmoles) of CsF, CH_3CN (3 ml) and PF_3O (2.84 mmoles) were added. The reactor was heated to 50° while stirring. After 24 hr the CH_3CN and excess PF_3O were pumped out. The weight increase of the salt phase indicated the absorption of 2.52 mmoles of PF_3O or 82.6% yield. Analysis revealed the pressure of equal quantities of the fluorophosphate ions indicated above.

Reaction between CsF and SF_4O.—Charges consisting of 0.717 g (4.75 mmoles) of CsF, 3 ml of CH_3CN, and 5.27 mmoles of SF_4O were placed together in the reactor in the same way given above. The mixture was stirred for 72 hr at room temperature and then the resulting solid was pumped to dryness. The weight of the solid corresponded to the addition of 3.58 mmoles of SF_4O or 76.2% yield. Upon prolonged pumping at room temperature, trace quantities of SF_4O were found to evolve from the solid. The spectral data given below suggest that the SF_5O^- ion has been formed.

Reaction of Alkali Metal Fluorides with PF_3S. A. CsF.—Cesium fluoride (0.449 g, 2.96 mmoles), CH_3CN (3 ml), and PF_3S (3.08 mmoles) were stirred together at ambient temperature for 72 hr and then the volatile phase was removed. The absorption of PSF_3 was 100% with respect to the amount of CsF used. To separate the $PF_2S_2^-$ ion from the PF_6^-, 50 ml of absolute ethanol was added. The undissolved portion contained $CsPF_6$, and the solution was filtered within a nitrogen-atmosphere drybox. Anhydrous ether was added to the ethanolic solution until it became cloudy and the mixture was allowed to stand at 0° for 3 hr. The solid which separated from solution was filtered and contained mostly $CsPF_6$ along with a small quantity of $CsPF_2S_2$. This process of fractional crystallization was continued several times until only $CsPS_2F_2$ was present in the solid. The solution phase was then pumped to dryness and the white solid deposit (needles) was washed several times with ether. *Anal.* Calcd for $CsPF_2S_2$: Cs, 50.0; F, 14.3; P, 11.6. Found: Cs, 50.3; F, 14.3; P, 11.9. The compound decomposed above 298°, somewhat lower than previously reported.[6]

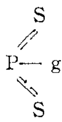
B. KF.—Potassium fluoride, CH_3CN, and PF_3S were loaded into the reactor in the quantities 1.01 g (17.4 mmoles), 3 ml, and 18.5 mmoles, respectively. The resulting mixture was stirred for 72 hr at ambient temperature. The solid was pumped upon until constant weight was achieved which corresponded to 98.9% conversion to KPS_2F_2 and KPF_6. The KPS_2F_2 was purified by the above method. *Anal.* Calcd for KPF_2S_2: K, 22.7; F, 22.1; P, 18.0. Found: K, 23.1; F, 22.3; P, 18.2; dec pt >260°.

Reaction between KF and PCl_3S.—The reaction mixture—KF (15.0 g, 0.258 mmole), CH_3Cl (20 ml), and PCl_3S (0.0643 mole)—was placed into a 150-ml stainless steel cylinder containing a dozen $^3/_8$-in. diameter stainless steel balls and the cylinder was shaken for 24 hr. Infrared spectral examination of the vapor phase revealed a small amount of PF_3S was present. The cylinder was shaken for an additional 24 hr and no PF_3S remained. Infrared and nmr analysis revealed the presence of KPF_2S_2 and KPF_6 salts after removal of the CH_3CN. The KPF_2S_2 was extracted by dissolution in 100 ml of ethanol and the small amounts of dissolved KPF_6 were removed in the manner given above; however, after recrystallizing twice in ethanol–ether mixtures, traces of chloride were still present with the KPF_2S_2. Consequently, the above methods are more convenient if pure alkali metal difluorodithiophosphates are desired. The recovery of KPS_2F_2 was 3.21 g or 58.4%.

Preparation of $(C_6H_5)_4AsPF_2S_2$.—Equimolar quantities of $(C_6H_5)_4AsCl$ and $CsPS_2F_2$ (2.41 mmoles) were added to 30 ml of absolute ethanol, and a solid consisting of $(C_6H_5)_4AsPF_2S_2$ and CsCl settled out of solution. After stirring for 3 hr the solids were filtered and then extracted with 50 ml of CH_2Cl_2 while stirring for 18 hr. Ether was added to the CH_2Cl_2 solution until the solution became cloudy. After allowing the small amounts of solids to settle, they were filtered and discarded. The liquid phase was pumped out and the remaining $(C_6H_5)_4AsPF_2S_2$ was washed several times with ether. The recovery was 0.783 g (63.1%). *Anal.* Calcd for $(C_6H_5)_4AsPS_2F_2$: C, 55.8; H, 3.9; F, 7.4. Found: C, 54.8; H, 3.94; F, 7.2; dec pt 270–275°.

Preparation of $[(C_6H_5)_3P]_2NPF_2S_2$.—The preparation was accomplished by adding 4.2 g of $CsPS_2F_2$ dissolved in 50 ml of ethanol to 9.1 g of $[(C_6H_5)_3P]_2NCl$ in CH_2Cl_2. The solids that were formed were filtered and then extracted in 100 ml of CH_2Cl_2. The resulting solution was refiltered and then concentrated to 50 ml. Ether (100 ml) was added and the resulting mixture was cooled to 0° for 18 hr. The solid was removed by filtration and 8.7 g of $[(C_6H_5)_3P]_2NPS_2F_2$ was recovered, corresponding to 82% yield. *Anal.* Calcd for $[(C_6H_5)_3P]_2NPS_2F_2$: C, 64.4; H, 4.47; N, 2.09; F, 5.7. Found: C, 64.8; H, 4.71; N, 2.13; F, 5.9; mp 222–225°.

Infrared Spectra.—The spectral properties of the $PF_2S_2^-$ ion have not been reported. Bands assigned to the P–F stretching frequencies are found at 818 (s) ν_{as} and 805 cm^{-1} (s) ν_s in the spectrum of $CsPS_2F_2$ while the spectrum of the potassium salt shows only a single broad absorption near 805 cm^{-1} (s). The PF_2S_2 group of the salts containing the above-mentioned complex cations have greater splitting of the bands associated with the P–F stretching motions as well as a shift to a slightly longer wavelength. For example, the spectrum of $(C_6H_5)_4AsPS_2F_2$ shows these absorptions at 804 (s) and 781 (m) cm^{-1}. When the cation is exchanged for the bis(triphenylphosphine)immonium ion, stretching motions due to the PF_2 group are found at 800 (s) and 771 (ms) cm^{-1}. When the sulfur atoms are replaced by oxygen, the P–F stretching motions are shifted to shorter wavelengths, *viz.*, at 814 and 797 cm^{-1} in the spectrum of $(C_6H_5)_4AsPF_2SO$.[9] Upon further oxygen substitution the shift is again increased, *e.g.*, to 850 and 835 cm^{-1} in the spectrum of KPF_2O_2. Such a shift is in the expected direction because a decrease in electron density in a nonmetal–fluorine bond normally causes a stretching frequency increase.

The bands assigned to the  group are at 735 (sh) and 710 (vs) cm^{-1} in the spectrum of $CsPF_2S_2$ and at 718 (s) cm^{-1} in that of KPF_2S_2. In the cases of the tetraphenylarsonium and bis(triphenylphosphine)immonium salts absorptions due to P=S stretching vibrations are located at 740 (obscured by the phenyl group absorption) and 725 (vs) cm^{-1} and at 740 (w–m) and 720 (vs) cm^{-1}, respectively. The P=S stretching vibration bands of salts containing the P_2F_2SO anions are found in the 618–645-cm^{-1} region.[9] The difluorodithiophosphate anions also show medium-intensity bands at 385 and 360 cm^{-1} and, in addition, at 318 (w) cm^{-1} in the cases of the potassium and cesium salts. These latter three absorptions are in the domain assigned to PF_2 bending motions.[10]

The spectrum of the SF_5O^- ion is relatively nondiagnostic. It contains a very strong, broad, and complex band centered at 718 cm^{-1} which is in the region associated with S–F and S–O stretching vibrations. Other absorptions are located at 600, 498 (m), and 470 (s) cm^{-1}. These three latter bands are *ca.* 100 cm^{-1} lower than the corresponding three in SF_5NF_2 and SF_5Cl which are assigned to the SF_5 group.[11]

^{19}F Nmr Spectra.—The spectrum of $CsPF_2S_2$ shows a doublet centered at ϕ 2.4 having a splitting value of 1164 cps. These values are in general agreement with those reported by Roesky, *et al.*[6] The splitting is somewhat larger than that of the $PF_2O_2^-$ ion (J = 952 cps), whose resonance is centered at ϕ 78.4. The δ and J values for the PF_2SO^- ion are intermediary.[9] The larger phosphorus–fluorine splitting in the spectrum of $PF_2S_2^-$ than in that of $PF_2O_2^-$ may be explained by the enhanced electron density in the P–F bond in the former.

The spectrum of the SF_5O^- ion shows a typical AB_4 pattern

---

(9) H. W. Roesky, *Chem. Ber.*, **100**, 950 (1967).

(10) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3279 (1966).

(11) G. A. Cady, D. F. Eggers, and B. Tittle, *Proc. Chem. Soc.*, 65 (1963).

very similar to the textbook example.[12] Resonances for the two sets of multiplets of the B_4 fluorine atoms are located at ϕ -92.9 and -96.9. The nine absorptions[13] for the A fluorine atom are centered at ϕ -130.7, -134.5, -135.3, -138.3, -138.8, -139.6, -142.6, -143.3, -146.9. The average $J \cong 160$ cps for the A fluorine nucleus and $J = 162$ for the B_4 nuclei.

Stability of $CsPF_2S_2$ toward Hydrolysis.—A saturated DMSO solution of $CsPF_2S_2$ was prepared. The solution was combined with an equal volume of water, and the ^{19}F nmr spectrum of the resulting mixture showed no reaction after 7 hr. Also, there was no reaction within the same length of time when *ca.* 0.1 *N* HCl solution was substituted for the water.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DAAH01-67-C-0655.

[12] K. B. Wiberg and B. J. Nist, "Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 565.

[13] H. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 340.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98105

New Preparation of Difluorocarbamyl Chloride, $ClC(O)NF_2$

BY RONALD L. CAUBLE AND GEORGE H. CADY

Received June 12, 1967

While $ClC(O)NF_2$ has been prepared by the reaction of Al_2Cl_6 with $FC(O)NF_2$,[1] it may also be obtained by irradiating N_2F_4 and $(ClCO)_2$ with Pyrex-filtered ultraviolet light.

In a typical run, 12 mmoles of $(ClCO)_2$ and 18 mmoles of N_2F_4 were held in a 2-l. glass bulb with a finger containing a medium-pressure, 350-w, water-cooled mercury lamp, and irradiated for 2 days. The flask then contained in decreasing amounts $COCl_2$, $ClC(O)NF_2$, CO_2, *cis*-N_2F_2, COClF, N_2F_4, SiF_4, HNF_2, COF_2, and N_2O. All known compounds were identified by their characteristic infrared spectra. About 20% of the $(ClCO)_2$ was converted into $ClC(O)NF_2$, which was purified by fractional codistillation.[2]

The average molecular weight of the pure compound obtained from vapor density measurements was 115.3 g/mole (calcd for $ClC(O)NF_2$, 115.5).

The F^{19} nmr spectrum was taken on a Varian Associates high-resolution, 40-Mc nuclear magnetic resonance spectrometer with a Model No. V-4311 fixed-frequency radiofrequency transmitter using 65 mole % CCl_3F as an internal standard. The spectrum showed a single, broad band at -41.8 ppm. This is close to Shreeve and Fraser's[1] value of -40.4 ppm which employed an external standard.

The infrared spectrum was taken at gas pressures ranging from 1 to 100 mm using a Beckman IR10 spectrometer and a Monel cell equipped with silver chloride windows, having a length of 10 cm. The infrared spectrum (in cm^{-1}) is: 3629 (vw), 1975 (vw), 1845 (vs), 1800 (s), 1117 (vw), 1071 (m), 947 (s), 910 (vvs), 770 (w, doublet), 645 (m, doublet), 521 (w), 474 (vvw). These values agree to within 5 cm^{-1} with those reported by Shreeve and Fraser.[1]

When water vapor was placed in an infrared cell along with difluorocarbamyl chloride the following reaction occurred

$$ClC(O)NF_2 + H_2O \longrightarrow HCl + HNF_2 + CO_2$$

All products were identified by their characteristic infrared spectra.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research. The nmr spectrum was acquired by B. J. Nist.

[1] G. W. Fraser and J. M. Shreeve, submitted for publication.

[2] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

CONTRIBUTION FROM THE RICHARD BENBRIDGE
WETHERILL LABORATORY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

A Photochemical Preparation of 1,1,2,2-Tetrachloro-1,2-dimethyldisilane

BY DALE REEDY AND GRANT URRY

Received June 12, 1967

While 1,1,2,2-tetrachloro-1,2-dimethyldisilane long has been recognized as a major constituent of the "disilane fraction" produced in the course of the direct synthesis of methylchlorosilanes,[1-3] it so far has not been obtained in a pure state. This apparently is the consequence of the extreme difficulties encountered in attempts to separate the 1,1,2,2-tetrachloro-1,2-dimethyldisilane from 1,1,2-trichloro-1,2,2-trimethyldisilane also present in the "disilane fraction."[4] A procedure involving photochemical chlorination has been suggested as a means of obtaining 1,1,2,2-tetrachloro-1,2-dimethyldisilane in a "reasonably pure" state since 1,1,2-trichloro-1,2,2-trimethyldisilane chlorinates at a faster rate than the other disilane.[5]

We wish to report a simple and convenient means of obtaining this and other symmetrically substituted disilanes in a high degree of purity with no difficult separation problems.

The recent study by Gunning and his associates[6] of

[1] R. Smith-Johannsen (General Electric Co.), U. S. Patent 2,601,337 (1952); *Chem. Abstr.*, **46**, 9342*d* (1952).

[2] M. Kumada, M. Yamaguchi, Y. Yamaoto, J. Nakajima, and K. Shiina, *J. Org. Chem.*, **21**, 1264 (1956).

[3] J. Chassot, German Patent 1,031,519 (1958); *Chem. Abstr.*, **54**, 25968*b* (1960).

[4] K. Tarama, A. Taketa, M. Kumada, and M. Kuriyagawa (Tokyo Shibaura Electric Co.), Japanese Patent 13,010 (1960); *Chem. Abstr.*, **55**, 10319*d* (1960).

[5] M. Kumada, M. Ishikawa, and S. Maeda, *J. Organometal. Chem.* (Amsterdam), **2**, 478 (1964).

[6] M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).