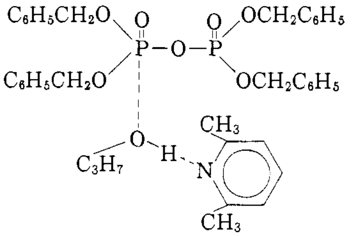
$$(C_6H_5CH_2O)_2 PO\cdot\overset{+}{N}R_3 + C_3H_7OH \longrightarrow (C_6H_5CH_2O) PO\cdot OC_3H_7 + R_3\overset{+}{N}H \quad (8)$$

A second possibility is that the reaction consists of a direct attack by propanol upon the phosphorus–oxygen bond and that the reaction rate is enhanced by the simultaneous attack of the base on the proton of the alcohol. If this mechanism is correct, the activated complex for the reaction would have the structure



Probably both mechanisms obtain in special cases (see below). But the reactions catalyzed by collidine and lutidine are most probably of the second type. For the data of Table IV and of Fig. 2 show that the catalysis by collidine and lutidine is diminished by a factor of about three when the reactions are carried out in C_3H_7OD rather than in C_3H_7OH as solvent. Presumably, therefore, a hydrogen–oxygen bond is broken in the rate-controlling step of the reaction. Since the reaction rate depends upon the concentration of the nitrogen base present in the solution, the activated complex shown above is most probably correct. This mechanism is at least roughly analogous to that postulated by Cunningham[21] for the action of chymotrypsin and might perhaps also serve as a model for a similar mechanism[22] for the action of phosphoglucomutase. However, pyridine, which is a weaker base than its homologs, causes a greater increase in rate. The details of this reaction have not yet been worked out, but the fact that the weaker base is the stronger catalyst suggests a different mechanism, which may prove to be a direct attack[2] of the base on phosphorus. However, neither the work with pyridine nor that with other unhindered bases (*e.g.*, imidazole) is yet complete.

Finally, the reaction in the presence of pyridine (and other) bases is strongly catalyzed by polyvalent cations. The salt effect on the reaction by sodium and potassium ions is not marked (see Table II) and that by the tetrabutylammonium ion is negligible. But lithium perchlorate strongly increases the rate, and ions such as calcium and magnesium are strong catalysts. These metal ion effects parallel those reported by Lowenstein[23] for the phosphorolysis of adenosine triphosphate and are analogous to enzymatic reactions of ATP, where magnesium ion is required for activity. The mechanisms of these processes are under investigation.

NOTE ADDED IN PROOF.—Professor H. C. Brown suggested, as an alternative explanation for the results with C_3H_7OD, that the amine might be much more strongly hydrogen-bonded in the deuterated than in the normal solvent. The kinetic results would then follow provided only the free-base were catalytically active. However, Mr. Robert Blakely has now found that the heats of solution of pyridine and of 2,6-lutidine in D_2O differ by less than 50 calories from the corresponding values in water. The alternative explanation is therefore considered untenable.

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CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Preparation and Properties of Pentafluoroselenium Hypofluorite (F_5SeOF) and Bis-(pentafluoroselenium) Peroxide ($F_5SeOOSeF_5$)

BY GRIHAPATI MITRA AND GEORGE H. CADY

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The fluorination of selenium dioxide and of selenium oxychloride has been found to give rather small yields of the new compounds, pentafluoroselenium hypofluorite (F_5SeOF) and bis-(pentafluoroselenium) peroxide ($F_5SeOOSeF_5$). The former is highly reactive. It boils at about −29° and melts at about −54°. The latter is relatively inert chemically. It melts at −62.8° and boils at 76.3°.

Although only one oxyfluoride of selenium, $SeOF_2$, has been described in the literature,[1–5] it appears probable that its close relationship to sulfur should permit selenium to form several oxyfluorides. Recent studies of the synthesis of SF_5OF, SO_3F_2, SOF_4 and $S_2O_6F_2$ by the fluorination of SO_3, SOF_2 and SO_2[6–9] suggest that similar fluorinations of SeO_2, $SeOF_2$ or $SeOCl_2$ may lead to the formation of new compounds of selenium, oxygen and fluorine. This expectation is strengthened by the

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fact that the compound $Te_3F_{14}O_2$ and possibly $Te_6F_{26}O_5$[10] have been produced by the fluorination of mixtures of TeO_2 and Te.

In accord with expectation, it has been found that the reaction of fluorine with selenium dioxide produces not only $SeOF_2$ and SeF_6 but also at least two volatile oxyfluorides. One of these is pentafluoroselenium hypofluorite, F_5SeOF and another is bis-(pentafluoroselenium) peroxide. There is some indication that an oxyfluoride containing three atoms of selenium per molecule is also produced. The fluorination of $SeOCl_2$ also gives $SeOF_2$, SeF_6 and $F_5SeOOSeF_5$.

Preparations

The Fluorination of Selenium Dioxide.—Dry selenium dioxide was pulverized in a mortar and was placed in a nickel boat capable of holding about 15 g. of the powder. One or two loaded boats were placed in a nickel tube which could be heated electrically. At the outlet end of the tube there was a short length of copper tubing which had been fastened to the nickel by silver solder. A moderate amount of the solder was on the inner wall of the copper tubing. During a fluorination run a mixture of fluorine and nitrogen entered the nickel tube at one end, passed over the selenium dioxide and, after leaving the tube, passed through a glass trap cooled externally by liquid oxygen. Products of the reaction collected in the trap. These products included substances formed by reaction of the stream of gas with Pyrex glass tubing at the inlet to the trap.

In all cases fluorine was used in such excess that unreacted fluorine emerged from the condenser trap. The results obtained under various working conditions follow. (1) At temperatures of 150 to 200° nearly all of the fluorine was consumed by reaction. At least 95% of the selenium dioxide was converted to selenium hexafluoride. (2) At a temperature of 120° nearly all of the fluorine in a slow stream of the gas was consumed with the formation of $SeOF_2$ and some SeF_6. (3) At temperatures of 90 to 150° a rapid stream of fluorine (10 to 12 l. per hr.) diluted by nitrogen resulted in excess fluorine passing through the system. The yield of SeF_6 was high and it contained some (about 5%) $SeOF_6$. (4) Fluorination at 60 to 90° yielded in addition to SeF_6 and $SeOF_6$ the compound $Se_2O_2F_{10}$ and another which may have been an oxyfluoride containing three atoms of selenium per molecule. (5) At temperatures below 40° prolonged fluorination of selenium dioxide with an excess of fluorine diluted well by nitrogen resulted in the formation of $SeOF_2$ and SeF_6.

Detailed descriptions of two fluorination processes follow. (1) 18 g. of selenium dioxide was fluorinated completely at 120°, the rate of flow of fluorine being 8 l. per hr. and of nitrogen 1.5 l. per hr. The product was separated into two fractions by allowing the trap to warm slowly to $-25°$, the portion which distilled being condensed in a second trap. The less volatile of the fractions weighed about 2 g. and the material was found to be largely the compound $Se_2O_2F_{10}$. The more volatile fraction was separated by distillation into SiF_4, SeF_6 (about 24 g.) and $SeOF_6$ (about 1 g.). (2) 32 g. of SeO_2 was fluorinated at 80°, the rates of flow of fluorine and nitrogen being 4 and 2 l. per hr., respectively. The product was separated by distillation into SiF_4, SeF_6 (about 8.5 g.), $SeOF_6$ (about 8.5 g.), $Se_2O_2F_{10}$, a liquid oxyfluoride which may have contained three atoms of Se per molecule and a small amount of a white substance, solid at room temperature.

As a fluorination reaction progressed the material in the nickel boat became a fluid paste, probably because of the presence of $SeOF_2$.

After the above work had been completed the reactor tube was remodelled. The exit tube of copper and its liberal supply of silver solder were removed. An exit tube of Monel metal was installed. Fluorination reactions using this apparatus again yielded a fluid paste in the nickel boat (which was consumed as the reaction progressed) but the product collected in the trap contained almost no $Se_2O_2F_{10}$. It contained much SeF_6 and some $SeOF_2$. The yield of $Se_2O_2F_{10}$ was greatly increased by again changing the reactor tube. A roll of silver-plated copper screening was inserted into the heated portion of the nickel reactor on the down-stream side of the nickel boat. This body of "catalyst" of the type found useful for many fluorination reactions was also helpful in this case. In a run with the reactor at about 110° an 8-g. sample of SeO_2 was treated for 1.5 hr. with a mixture of equal volumes of F_2 and N_2 flowing at a rate of 6 l. per hour. The product in the trap contained about 1.6 g. of $Se_2O_2F_{10}$ and little if any $SeOF_2$. There was also no indication of an oxyfluoride containing three atoms of selenium per molecule.

In one run made with the remodelled reactor at about room temperature and with no catalyst present an explosive substance was formed. The explosion occurred when the trap had warmed to about 0°.

Fluorination of $SeOCl_2$.—Details of one fluorination reaction follow: a 22-g. sample of $SeOCl_2$ was fluorinated in a nickel boat in the first reactor used with selenium dioxide. As the reactor was warmed slowly to 50° fluorine diluted by nitrogen was passed. A mixture of chlorine (and perhaps some ClF) and selenium hexafluoride (total weight of product, 12 g.) collected in the cold trap. The temperature of the reactor was increased to 75° and as the diluted fluorine (8 l. per hr. of F_2, 2 l. per hr. of N_2) passed, the product was condensed in a second cold trap. Upon distillation the product in the second trap was found to contain traces of Cl_2 and $SeOF_6$. The principal product was SeF_6 and the second most abundant product was $Se_2O_2F_{10}$. The remodelled reactor also failed to give much $Se_2O_2F_{10}$ until the body of catalyst was added.

Fluorination of $Se_2O_2F_{10}$.—The action of fluorine upon $Se_2O_2F_{10}$ at 70° in the first reactor yielded a mixture containing about 78% SeF_6 and 18% $SeOF_6$.

Separation of Products.—SiF_4, formed from the glass trap, was largely removed from the product by allowing the trap to stand at the temperature of subliming carbon dioxide.

SeF_6 was very difficult to separate from *$SeOF_6$* because the former sublimed and could not be separated using a conventional fractional distillation column at one atmosphere pressure. A process of fractional sublimation at low pressure finally was used with success to obtain a small sample of $SeOF_6$. The method will be described in another article by one of the authors.

$Se_2O_2F_{10}$ was obtained either by fractional distillation under reduced pressure (for example, about 205 mm. at 41.2°) or by a simple bulb to bulb distillation. In the latter case it was necessary to evaporate most of the sample before the distillate was pure $Se_2O_2F_{10}$.

The liquid which may have been an oxyfluoride containing three atoms of Se per molecule distilled at about 60° under a pressure of 18 mm.

Analyses.—Each of the compounds was analyzed for selenium and fluorine. $SeOF_6$ hydrolyzed quantitatively in a solution of potassium hydroxide. The other materials were decomposed by fusing with metallic potassium. Aqueous solutions of the products were divided into two parts. Selenium was estimated as metallic selenium by reducing one part of the solution with hydrazine hydrochloride after the removal of fluoride ions. The other part was used for the estimation of fluorine as calcium fluoride. *Anal.* Calcd. for $SeOF_6$: Se, 37.75; F, 54.54. Found: Se, 37.23, 37.01; F, 54.68, 54.31. Calcd. for $Se_2O_2F_{10}$: Se, 41.56; F, 50.01. Found: Se, 41.09, 41.03; F, 49.39, 49.52. Calcd. for $Se_3O_2F_{14}$: Se, 44.26; F, 49.72. Found, for the material which might contain three atoms of Se per molecule: Se, 44.88, 44.92; F, 49.13, 49.20.

Chemical Properties of the Compounds. $SeOF_6$.—Of all of these compounds pentafluoroselenium hypofluorite was found to be by far the most reactive. It reacted with water to set free oxygen. A known weight of pentafluoroselenium hypofluorite was allowed to react with a solution of potassium hydroxide of known strength. The reaction was strongly exothermic. The volume of the gas left after the reaction was approximately equal to half the volume of the initial sample measured at the same temperature. The mass spectrum as well as the molecular weight of this residual gas proved it to be oxygen. Two reactions were possible in this case.

$$2SeOF_6 + 16KOH = 2K_2SeO_4 + 12KF + 8H_2O + O_2 \qquad (1)$$

$$2SeOF_6 + 12KOH = 2KSeO_3F + 10KF + 6H_2O + O_2 \qquad (2)$$

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[10] R. Campbell and P. L. Robinson, *J. Chem. Soc.*, 3454 (1956).

The solution left after the reaction was titrated quickly with an acid to determine the amount of KOH consumed. The result of titration indicated that about 85% of the compound was acted upon according to equation 1. The corresponding compound of sulfur under similar conditions is known to give only fluorosulfonate ion. This is in keeping with the stability of the latter compared to that of the fluoroselenate ion.[11] Gaseous $SeOF_6$ liberated iodine instantaneously from a solution of potassium iodide; selenium hexafluoride did not. In an acid solution selenium was reduced by iodide to different oxidation states including that of elementary selenium; hence, the reaction of potassium iodide solution could not be used in a quantitative analysis. Even traces of water vapor reacted with pentafluoroselenium hypofluorite. The structure of this compound probably is F_5SeOF. The odor of this compound was strong and irritating. In general it seemed to be reasonably stable. On one occasion when a sample which had been prepared by fluorinating $Se_2O_2F_{10}$ was allowed to warm quickly it exploded with violence.

$Se_2O_2F_{10}$.—Bis-(pentafluoroselenium) peroxide was found to be almost inert toward water and toward concentrated solutions of sulfuric acid or sodium hydroxide. It reacted very slowly with a solution of potassium iodide. Anhydrous calcium chloride did not react and sulfur reacted only on warming. It reacted very quickly with benzene, α-naphthylamine and pyridine, producing strongly colored products. Similar observations have been made in connection with Te_2F_{10} and $Te_3O_2F_{14}$ by previous workers.

When heated to 200° in a closed copper tube it decomposed to give selenium hexafluoride and other products (not identified). An attempt was made to store the material in a copper vessel at room temperature. After one month none of the original compound remained in the container. Other samples stored in Pyrex glass showed little or no decomposition after three months. The glass was etched somewhat.

A sample of the liquid thought to contain three selenium atoms per molecule decomposed when heated to 250° yielding SeF_6 and other products.

Physical Properties of the Compounds. Melting Points.—The observed melting points for SeF_5OF, $Se_2O_2F_{10}$ and for the liquid thought to be a higher oxyfluoride were, respectively, -54, -62.8 and about $-20°$.

Molecular Weights.—The average experimental values obtained for the molecular weights (by vapor density) of these compounds were 208.5 for $SeOF_6$; 378 for $Se_2O_2F_{10}$. Because of the very low vapor pressure of $Se_3O_2F_{14}$, accurate vapor densities were not established. A few experiments suggested the molecular weight to be in the vicinity of 520. Theoretical values for these compounds are, respectively, 208.9, 379.9 and 534.9.

Vapor Pressures and Boiling Points.—Vapor pressures of $SeOF_6$ and $Se_2O_2F_{10}$ are given in Tables I and II. The values must be regarded as rather crude, because the samples were small and possibly not of high purity.

Mass Spectra.—The mass spectra of $SeOF_6$ and $Se_2O_2F_{10}$ were very complex and much alike. They both gave evidence for the ions Se^+, SeF^+, $SeOF^+$, SeF_2^+, $SeOF_2^+$, SeF_3^+ and SeF_5^+. From $Se_2O_2F_{10}$ weak lines were observed for SeF_4^+ and $SeOF_3^+$.

Infrared Spectra.—The infrared absorption spectra of these gases were measured over the range 2–15 μ by means of a double beam Perkin–Elmer spectrometer, model 21. A glass cell of 10 cm. length equipped with sodium chloride windows was used, pressures of the gases being 25 mm. or less. The spectrum for F_5SeOF was very simple. It had a weak band at 925 cm.$^{-1}$ which may have been due to O–F stretch. The O–F absorption frequency has appeared at about this frequency in other compounds.[12] There was also a weak absorption at 842 cm.$^{-1}$. A very strong and broad absorption with a maximum at 758 cm.$^{-1}$ corresponded to Se–F stretch. The spectrum of $Se_2O_2F_{10}$ consisted of very strong absorptions at 737, 762 and 775 cm.$^{-1}$, strong absorptions at 722 and 842 cm.$^{-1}$, a moderate absorption at 858 cm.$^{-1}$ and weak absorptions at 1295 and 1405 cm.$^{-1}$. The strongest absorption probably resulted from Se–F stretch, a frequency of 780 cm.$^{-1}$ being known for SeF_6.[13]

TABLE I

VAPOR PRESSURE OF $SeOF_6$

T, °K.	P, mm.	T, °K.	P, mm.
220.9	229.3	235.6	505.3
223.1	250.1	237.8	560.1
224.6	273.8	238.7	609.6
225.9	296.3	239.5	640.0
227.9	342.1	240.4	640.9
231.5	402.2		

TABLE II

VAPOR PRESSURE OF $Se_2O_2F_{10}$

T, °K.	P, mm.	T, °K.	P, mm.
301.9	116	327.8	351
305.9	140	331.5	404
310.1	169	337.5	500
314.6	205	342.4	599
319.1	249	349.1	754
324.1	302	(349.4)	(760)

Absorption frequencies found in Raman spectra for 50% selenic acid, solid selenic acid and for solid $KHSeO_4$ have been known to occur, respectively, at 862, 896 and 852 cm.$^{-1}$.[14] These values suggest that the bands at 842 cm.$^{-1}$ in $SeOF_6$ and $Se_2O_2F_{10}$ may have been due to Se–O stretch.

N.m.r. Spectrum.—The nuclear magnetic resonance spectrum for $Se_2O_2F_{10}$ was studied using a Varian Model V 4300 B spectrometer. When the fluorine resonance was scanned rapidly a single strong line was observed indicating that the ten fluorine atoms were essentially alike and suggesting the structure $F_5SeOOSeF_5$. A slower rate of scanning broadened the peak and resolved it into a complex structure accounted for, at least in part, by the presence of Se^{77}.

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SEATTLE 5, WASHINGTON

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