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REACTIONS OF SOME GROUP VI ELEMENTS, OXIDE AND URANIUM WITH CHLORINE-HYDRO-GEN FLUORIDE MIXTURES

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To Professor George H. Cady on his 70th birthday

SUMMARY

When group VI elements and uranium were reacted with chlorine-hydrogen fluoride mixtures, good yields of WF₆ were found in the case of W, while only MoF₅, Mo^V chlorofluorides, and a spectroscopic trace of MoF₆ were found when the element was Mo. Uranium gives UF₄ at lower temperatures whereas at higher temperatures U₂F₉ and a spectroscopically-detected UF₆ were found. The reaction with SOF₂ always results in SO₂F. At higher temperatures SF₆ could be detected by spectroscopic means but not isolated. The predominant product with Se is SeCl₄. When WO₃ is reacted an oxyfluoride is formed.

INTRODUCTION

In the course of studying behavior in the anhydrous hydrogen fluoride solvent system, we investigated the parallel between the disproportionation behavior of halogens in HF and in water.

$C1_2 + H_2O = HOC1 + HC1$	(1)
$C1_2 + HF = FC1(C1F) + HC1$	(2)

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While the equilibrium in reaction (2) is far to the left, proper application of Le Chatelier's principle can shift it to the right, yielding ClF and HCl $\begin{bmatrix} 1 \end{bmatrix}$. While Br₂ and I₂ can disproportionate in an HF medium, the principal products are BrF₃ and IF₅, respectively, as well as halide $\begin{bmatrix} 2 \end{bmatrix}$. This demonstrates a rather pretty trend in the periodic table and is consistent with thermodynamic predictions.

When ClF reacts with some group VI elements $\begin{bmatrix} 3 \end{bmatrix}$, the products are SF₄, SeF₄, WF₆, and MoF₆ at room temperature. At 200^o the products were SF₆ and SeF₄. Chlorine was the other product.

An investigation was undertaken to see if one could fluorinate group VI elements and uranium by using "in situ"-formed ClF from mixtures of HF and Cl₂. The rationale was that if ClF is present in equilibrium with HF it might react with the group VI element. If that happened, Le Chatelier's principle would require the formation of more ClF which would further react.

Much of the thermodynamic drive would come from the free energy of formation of the group VI fluorides. An alternative rationale might be to think of chlorination of the group VI element followed by halogen exchange.

RESULTS AND DISCUSSION

The heats of reaction and free energies of elements with ClF and with Cl_2 mixtures at 298° are given in table I. These are calculated from the standard free energies and enthalpies of formation of the products shown in table II. The Cl_2 - HF - element reaction to form the hexafluorides, except for SeF₆, all appear to be favorable. It should be pointed out that we were working at far from standard states and under conditions where solvent effects may be significant.

Galculated Standard	nears and fre	e energies of	leaction	
Principal Product	$M + nClF = \Delta H (Kcal)$	$\frac{MFn + \frac{n}{2}Cl_2}{\Delta G (Kcal)}$	$M + \frac{n}{2}C1_2 + \Delta H (Kcal)$	nHF = MFn + nHC1 $\Delta G (Kca1)$
SF ₆	-208	-181	-39	-12
SeF ₄	-110	-94 minimum value	+9	+20 minimum value
wf ₆	-341	-314	-172	-145
Mof ₆	-308	-278	-123	-109

TABLE 1 Calculated standard heats and free energies of reaction

	M + nClF =	MFn + $\frac{n}{2}$ C1 ₂	$M + \frac{n}{2} C1_2 +$	nHF = MFn + nHCI
Principal Product	Δ H (Kcal)	Δ G (Kcal)	ΔH (Kcal)	Δ G (Kcal)
UF ₆	-436	-403	-269	-234
SeF ₆	-165	-141	+4	+30
UF4	-389	-366	-270	-253
U ₂ F9	-812	-760	-554	-507
UF5	-426	-389	-273	-248
MoF ₅	-263		-121	

TABLE 2

Standard free energies and enthalpies of formation from the elements

	Δ H _f , 298 (Kcal)	Δ G _f , 298 (Kcal)	Reference
^{SF} 6 (g)	-289	-264	4
^{SeF} 6 (g)	~246	-222	5
WF ₆ (1)	-422	- 397	6
MoF ₆ (1)	-389	-361	7
UF ₆ (s)	-517	-486	8,9
UF_4 (s)	-443	-421	9, 10
U_2^{F9} (s)	~934	-884	8,9
UF5	~484	-458	9, 10
^{MoF} 5 (s)	-332	~	11
WF5 (s)	-348		11
^{MoOF} 4 (s)	-330		11
WOF ₄ (s)	-359		11
SeCl4	-46	- 26	5
s ₂ c1 ₂	-14	~	12
sc1 ₂	-12		12
SeC12	-10		4, 13
Se ₂ C1 ₂	-22	-18	14
WO_2F_2 (g)	-215 (572*)		15
MoCl5 (s)	-126	-101	16
WO ₃ (s)	-201	-183	16
HOC1 (g)	-22		17

*∆H atomization

Compound	Δ H $_{ m f}$, 298 (Kcal)	Δ G $_{ m f}$, 298 (Kcal)	Reference
HOH (1)	-58	-56	18
C1F	-135	-13.8	4
HF	-64	-65	4
HC1	-22	-23	4

TABLE 2, cont'd.

The reaction between W and Cl₂ - HF mixture goes smoothly at 200° to give WF₆ in good yield. This parallels the reaction with neat ClF to give WF₆ [3]. When twice stoichiometric amounts of Cl₂ and HF were used, the yield based on WF₆ actually recovered after fractionation was 92%. No doubt some was lost when the more volatile products (HCl) were removed. Stoichiometric amounts gave lower conversion (ca. 74.5%). The reaction is consistent with thermodynamic prediction. The lower fluoride, WF₅, is unstable with respect to disproportionation.

The free energy change for the reaction of Cl_2 , HF and Mo to form MoF_6 is quite favorable (-99 Kcal/mole). However, no significant amounts of MoF_6 were found among reaction products. Indeed, no significant amount of any volatile halides of molybdenum were obtained until the reaction temperature was raised to 300° , the temperature where chlorine is known to chlorinate metallic molybdenum to $MoCl_5$ [19]. Molybdenum hexachloride is unknown. Since only MoF_5 and a mixture of Mo^V chlorofluorides were found in significant amounts, one might be tempted to conclude that the mechanism for the production of products involved the chlorination of Mo to $MoCl_5$ followed by halogen exchange with the HF. All of these mixed halides save brown $MoCl_2F_3$ are volatile solids and are quite soluble in HF. The hexafluoride was observed spectroscopically. It probably arose by the disproportionation of the pentafluoride to MoF_6 and MoF_4 . Neat ClF reacts nicely with the metal to give MoF_6 [3].

Considerable effort was expended attempting to get the reaction $U + 6 \text{ HF} + 3 \text{ Cl}_2 = UF_6 + 6 \text{ HCl}$ to go to completion. The free energy change for this reaction is quite favorable (-234 Kcal/mole). However, at 200^o metallic uranium is smoothly and quantitatively converted to UF₄ (ΔG = -253 Kcal/mole). This is a nice way to make ClF₄ from the metal, probably better than the reaction with neat HF at 250^o [20]. At temperatures between 400-600° some U_2F_9 ($\Delta G = -507$ Kcal/mole) identified from its x-ray powder pattern appeared, as did a spectroscopic trace of UF₆. Reactions carried out in the 400-600° range were in a reducing atmosphere since some hydrogen resulted from attack by HF on the metal apparatus. A closer look at the thermodynamic data points out that, while the formation of UF₆ is favorable, the formation of UF₄ (and U₂F₉) is even more favored. In this light, the lack of satisfactory yield of UF₆ is not surprising. However, UF₄ reacted with ClF to give UF₆.

Sulfur reacts with neat ClF at room temperature to give SF_4 and at higher temperatures to give SF_6 [3]. All known sulfur chlorides can be prepared from the element [21]. One might expect that the lower sulfur fluorides up to SF_4 might be formed by halogen exchange if not by reaction of "in situ"-formed ClF. Sulfur tetrachloride ($SC1_3^+C1^-$) is reported to be an unstable solid decomposing at -30° [22]. The more stable oxidation state for the chlorides is II, while IV and V are those for the fluorides. One might expect that if the mono- or disulfur fluorides were formed by halogen exchange a series of disproportionation reactions would lead to SF_4 as one of the reaction products. Experiments conducted during the work show that SF_4 is unstable toward HC1. This appears to be inconsistent with the reaction [23] to form SF_4 from NaF and $SC1_2$ which involves simply a halogen exchange and disproportionation. However, conditions are quite different. Thermodynamic data suggest that SF_4 should be stable toward HC1.

Since SOF_2 is a product of the reaction of SF_4 with moisture- or oxygen-containing specimens, its appearance in the products of every run could be interpreted to mean that some SF_4 was produced.

While the free energy change for the formation of SF_6 from S, Cl_2 and HF appears to be favorable (-12 Kcal/mole) there is not a strong driving force. Since SCl_6 has not been prepared, one should not expect a halogen exchange mechanism to give SF_6 . Several reaction schemes attempted between 350-600° resulted in spectroscopic evidence for SF_6 but no recoverable amounts were found. These higher temperature reactions were complicated by plug-ups and excessive corrosion on materials of construction.

While neat ClF will react with Se to give $\operatorname{SeF}_4[3]$, mixtures of HF and Cl₂ react with Se from 200-300° to give a mixture of SeCl_4 and $\operatorname{Se}_2\operatorname{Cl}_2$. Selenium tetrachloride is the predominant product. The $\operatorname{Se}_2\operatorname{Cl}_2$ probably arises from decomposition of SeCl_2 while removing unreacted volatiles from the mixture. Halogen exchange does not occur between SeCl_4 and HF but rather between SeF_4 and HCl. Estimated thermodynamic data would predict that the reaction would most likely give some SeF_4 or SeF_6 . Considerable effort was

devoted to isolating and identifying a mixed $\mathrm{Se}^{\mathrm{IV}}$ halide. This was not successful.

Since this work was completed, Lau and Passmore [24] have reported that neat ClF will react with SCl_4 at -78° and $SeCl_4$ at room temperature to give the tetrafluorides and chlorine. Small amounts of $SeClF_5$ were also found.

When ClF is reacted with WO₃, the products are WF₆, ClO₂F and Cl₂ [3]. Since tungsten in WO₃ is already in its highest oxidation state, no reduction products were expected in the reaction with Cl₂ and HF. We had hoped that the presence of excess HF would minimize hydrolysis leading to oxy-fluorides. Elemental analysis on the non-volatile solid residue led to the empirical formula WO₂F₂. Examination of the volatiles revealed the presence of HCl and H₂O. We had not anticipated finding HCl but realized that it could come about by the disproportionation of Cl₂ in water. We were unable to detect either HOCl or its anhydride, Cl₂O, spectroscopically or by vapor phase chromatography. Since WOF₄ is very susceptible to hydrolysis it is reasonable that WO₂F₄, rather than WOF₄, would be found in the presence of water. While the compound WO₂F₂ has been claimed much earlier it has been more recently prepared and characterized mass spectrometrically by heating a mixture of WO₃ and CrF₃ in a tantalum Knudsen effusion cell at 6000 [25].

While HF-Cl mixtures may prepare fluorides of some elements from appropriate compounds, it is clear that oxyfluorides will result in some cases where an oxygen function is present. This mixture is, however, a useful synthetic reagent. It may be that at lower temperatures (i.e., 200°) easilyfluorinated substances may form higher fluorides by the reaction of "in situ" -generated ClF in the manner proposed; the mechanism of reaction at higher temperatures may be that of chlorination followed by halogen exchange. Apparently not all of the compounds which can be prepared by reactions involving HF can be prepared using Cl₂-HF mixtures.

EXPERIMENTAL

Reactions carried out between 200° and 300° were in Hoke Monel highpressure cylinders. Occasionally a stainless steel cylinder was used. A few reactions were carried out where the heating was done via a cylindrical heating mantle or a sand bath. For some reactions the pressure was monitored by Bourdon tube gauge. Most reactions conducted at temperatures above 300° were carried out in a high-pressure Inconel reaction bomb (Parr Model 4653) whose heater (Parr Model 4925) took it to 600° C. However, it was soon discovered that in the neighborhood of 400° the alloy reacts with HF to liberate hydrogen.

In a typical reaction the reaction vessel was first passivated with $C1F_3$. After this was pumped out its tare weight was recorded. A small amount of weighed solid was added to the cylinder with the valve removed. After the valve was replaced it was reattached to a vacuum manifold, pumped down and cooled with liquid nitrogen. Appropriate amounts of HF and $C1_2$ were condensed in either from tared reservoirs or from calibrated expansion bulbs.

Usually the reaction vessel was weighed after each addition as an additional check. The reaction vessel was pumped on for approximately one hour while cooled with liquid nitrogen in order to outgas any air or other more volatile gases which may have been present. The vessel was then removed from the manifold, the exposed end of the valve sealed and heated for the desired time. After cooling, its weight was checked in order to determine if any leaks had occurred. It was then returned to the manifold. The parts of the manifold which had been exposed to air while connected were further treated with ClF₂ before the valve to the cylinder was opened.

The volatiles were usually recovered through three traps: the first was a 0° , -24° , or -77° ; the second a dry ice trap; the third a dry nitrogen trap. Co-distillation was also sometimes used. A useful gas chromatograph was not available to us in the earlier work. After we designed and constructed a special one it became quite useful.

A spot check on volatiles was taken by taking several fractions at 200 torr pressure in a Monel cell usually with silver chloride windows, scanning from 500 cm.⁻¹ to 4000 cm.⁻¹. All infrared data was taken on a Beckman IR-12 instrument.

After all volatiles were recovered (final heating was used) the vessel was weighed to determine the amount of solid residue. The vessel was then filled with dry nitrogen and was opened in a nitrogen-filled glove box. The solid was recovered, weighed, and properly stored until it could be hydro-lyzed in basic solution for elemental analysis. When infrared data was used it was taken as Nujol or Ke1-F-10 mulls on silver chloride windows.

Tungsten

When essentially stoichiometric amounts of reactants (slight excess of Cl and HF, 0.1155 moles W) were heated in a Monel cylinder at 200° for 17 hours the yield, based on amount of W converted to WF₆, was 74.5%. The WF₆

was identified by freezing point, molecular weight, vapor pressure and IR measurements. WF₆ shows a strong absorption band at 711 cm.⁻¹. The only other observed bands were for SiF₄, HCl and HF. Twice stoichiometric amounts of Cl₂ and HF (W 0.05775 moles) when heated for two hours at 200^o gave conversion of W to WF₆ at 92%.

Molybdenum

A 150 ml. Monel cylinder containing 6.22 grams (.0648 moles) of Mo, 10 grams (.50 moles) of HF, and 9.85 grams (.278 moles) of Cl_2 was heated to 200° for 20 hours. None of the fractions of the volatiles examined showed the strong IR stretching modes at 741 cm.⁻¹ or the two weak combination bands at 1385 cm.⁻¹ and 1480 cm.⁻¹ expected of MoF₆ [26, 27, 28]. They did reveal a very strong HCl band at 2800 cm.⁻¹. The Cl_2 used was optically free of HCl. A repeat of the experiment using 3 grams of Mo, 7.8 grams of Cl_2 , and 20 grams of HF in a 700 ml. stainless steel cylinder heated to 200° for 10 hours showed strong HCl bands. A sample examined at 130 torr pressure revealed a similar shoulder at 741 mm. and a large unidentified peak at 720 cm.⁻¹. A sample taken at 700 torr pressure showed a strong band at 741 cm.⁻¹. The weak combination bands were not observed. The HCl was collected from the bottle cooled to -78° . The HCl collected weighed 5.25 grams. For MoF₆ one expects 6.84 grams, for MoF₅ 5.70 grams.

A Monel vessel containing 0.08550 moles of Mo, 0.660 moles of HF, and 0.284 moles of HF was heated at 200° for 16 hours. All of the volatiles came off at -34° . Heating in steps to 200° removed no more volatiles. The weight of the residue remaining in the vessel was within 0.5% of that expected for conversion of Mo to MoF₆. Dry nitrogen was used to determine that the valve was not plugged. The vessel was recharged with Cl_2 and HF and heated to 250° for 17 hours. The IR spectra of solutions showed only HCl and HF bands. No residual volatiles were isolated. The vessel was attached to a Kel-F cooled trap and heated for 4 hours at 200° . When the vessel was opened to the atmosphere a piece of filter paper developed the blue color associated with lower oxidation states of Mo exposed to moisture. Examination of the fittings of the manifold showed that the material lost by the reaction vessel had deposited on the internal cool surfaces of the manifo.

The one-liter Inconel bomb containing 0.44 moles of Mo, 2.64 moles of HF, and 1.32 moles of Cl_2 was heated to a maximum temperature of 350° for a 14-hour period. The easily-removed volatiles were fractionated through a series of cold traps, #1 at -22°, #2 at -78°, and #3 at -196°. After this

the bomb was heated to 300° over a 24-hour period while a Ke1-F trap cooled with a dry ice bath was connected. After about 1 ml. of products were collected in the trap the bomb plugged and could not be unplugged in a manner which would allow for the recovery of the other products.

The Kel-F trap contained at room temperature a colorless liquid and a yellow solid. The liquid phase froze at about -76° . The yellow solid did not melt when placed in a hot water bath at 85° .

Nothing interesting was found in the #1 trap. The second, when warmed to nearly 0°, gave a mixture of a colorless liquid and yellow solid which condensed into another Kel-F trap at -76° . The vapor pressure and color suggest the liquid was HF. Both solid and liquid sublimed off together. When a portion was sublimed into an unpassivated Kel-F vessel the yellow solid decomposed within a few minutes to a light green solid. Overnight the solid became quite dark.

The one-liter Incomel bomb, containing 20 grams of Mo and a large excess of HF and Cl₂, was heated to 320⁰ overnight. After cooling to room temperature the volatiles were removed under reduced pressure through three traps connected in series, the first two at the dry ice temperature, the second at liquid nitrogen. The first was warmed to room temperature and its contents distilled into a Kel-F vessel where a solution of the yellow solid in HF resulted. Attempts to separate the portions of the mixture by trapto-trap distillation failed, as did codistillation from a 16" U-tube packed with copper shot.

The reaction bomb was recharged with Cl_2 and HF in order to use up any unconverted Mo. This was heated for 8 hours at 350° . The volatile products were collected as separated into two fractions as in the previous reaction. One fraction was unreacted Cl_2 and HCl; the second, unreacted IIF and volatile Mo halides. The second fraction was then fractionated into four solutions: 1. dark brown; 2. rust-brown (more red); 3. bright orange-red; 4. slightly yellow to colorless. The fourth gave a yellow solid when cooled to dry ice. The HF could be fractionated from #I but not the others. This left a dark brown solid. The yellow content of #4 was assumed to be essentially MoF₅ and the rest mixed Mo halides in the IV or VI oxidation state.

A portion of the yellow HF solution was adsorbed onto activated NaF held at 100° . The mixture was desorbed at 350° and readsorbed at 100° . This was repeated three times. The NaF trap was opened in a dry box and a Kel-F-10 oil mull prepared on an AgCl window. Its IR spectra revealed a sharp medium band at 605 cm.⁻¹ where MoF₆ in alkali metal hexafluoromolyb-dates absorb. A second portion of the yellow solution was placed into a

10 cm. IR cell with AgCl windows. The windows were chilled with dry ice while the cell was pressurized with 1500 torr NO_2F and allowed to stand for l_2^1 hours. The cell was then evacuated and the IR spectra recorded. A medium and sharp band at 613 cm.⁻¹ and a strong band at 1380 cm.⁻¹ and some unidentified bands were observed. The band at 613 cm.⁻¹ [29] has been shown, using a similar technique, to be caused by MoF₆ in MOMoF₆. The band at 1380 is NO_2 [29, 30]. A band around 2350 cm.⁻¹ [30] due to NO_2^+ in NO_2MOF_6 was expected but not seen in this scan. The sample rapidly decomposed off the window units. The cell became filled with NO_2 . The band at 613 cm.⁻¹ decreased in intensity. This probably explained why the NO_2^+ band was missed. When the cell was evacuated and a second deposit on the window was made, a weak band which rapidly decomposed was found at 2362 cm.⁻¹. The yellow **ap**-parently was MoF₅.

Uranium

In order to have a basis for comparing reactions of Cl_2 -HF mixtures with those of C1F on U, 0.5 grams (.0016 moles) of UF₄ and 3.3 grams of C1F were loaded into a 150 ml. Monel cylinder and heated to 300° for 15.5 hours. The IR spectra of the two samples of the volatile component of the reaction mixture showed a strong band at 624 cm.⁻¹. The reaction vessel was cooled to 0° and the volatile compounds distilled off into a liquid-nitrogen-cooled trap. The remaining fraction was allowed to warm to room temperature. The spectrum taken at 127 torr resulted in essentially pure UF₆ with absorption bands at 624vs, 674s, 715w, 825m, 1159m and 1288 cm.⁻¹¹ [31, 32].

A second run with 5 grams of UF₄ and 12.6 grams of C1F was held in a 300 ml. Monel cylinder at 300° for 16 hours. The recovered C1F, Cl₂ and UF₆ indicated essentially quantitative conversion. SiF₄ was also observed in the IR.

A 300 ml. Monel cylinder containing 31.8 grams (0.133 moles) of U, 0.399 moles of Cl_2 and 0.798 moles of HF was heated to 300° for 18 hours. The vessel was cooled to 0° and the volatiles (essentially HC1) removed. The weight of the volatiles (HC1) was that expected for quantitative conversion of U to UF₄. When the vessel was heated to 50° the infrared spectrum of the volatiles did not suggest UF₆. The weight of the non-volatile was that expected for a conversion of U to UF₄. The vessel was recharged with 0.266 moles of HF and 0.133 moles of Cl_2 and heated an additional 15 hours. The infrared spectra of a sample of the volatiles revealed a very weak signal for HCl and none for UF_6 . The weight of the reaction vessel and residue had not changed beyond experimental error. The vessel was then recharged with HF and Cl₂ and heated for an additional seven days, the last six hours of which were at 350°. The rest of the time the temperature was 300°. The volatiles revealed a very weak HCl signal and none for UF₆ in the IR. The x-ray powder pattern on the green solid which was removed from the vessel was that of UF₄.

Many variations on the scheme were tried at temperatures as high as 700° . A flow system was tried as well as schemes where AgF was present in order to increase the fluorine ion concentration, to act as a chloride and to lead to the possibility of a silver complex containing U^{VI} . At higher temperatures, x-ray powder patterns showed the presence of U_2F_9 in the residue and UF₆ was detected spectroscopically (IR) but no recoverable amounts of UF₆ were found. There was some, but not conclusive, evidence of a silver complex. Silver was sometimes found as AgCl. Metallic silver was also found in high-temperature reactions, perhaps arising from H₂ formed by HF attack on Inconel or by direct reduction by Inconel of AgF.

Sulfur

A 150 ml. Monel cylinder containing 1.430 grams (0.4460 moles) of S, 20 grams (1.0 moles) of IIF and 12.3 grams (.173 moles) of $C1_2$ was heated for 20 hours at 200°. The cylinder was cooled to dry ice temperature and 2.2 grams of HC1 were distilled off under reduced pressure. A fraction taken for analysis by IR showed 11 bands interpreted as arising from SOF₂ and a SiF₄ band at 1030 cm.⁻¹. The low conversion to HC1 (2.2 grams) was in the neighborhood of that which would be expected if considerable conversion of sulfur to SOF₂ occurred. No bands associated with SF₄ or SF₆ were observed. Cylinder and contents returned to the tare weight when all volatiles were removed. Therefore, the remainder was unconverted sulfur. Similar results occurred when 1.4 grams (.044 moles) of sulfur, 25 grams (1.3 moles) of HF, and 14.5 grams (.204 moles) of Cl₂ were heated in a 300 ml. stainless steel vessel at 250° for 36 hours. Infrared spectra were taken of fractions taken at -78° , -36° , and room temperature.

To increase the basicity of the medium 1.450 grams (.04523 moles) of sulfur were added to the stainless steel cylinder containing 32.55 grams of a solution of NaHF₂ (4.188 grams/100 ml.) in HF and 18.4 grams of Cl₂ was condensed in. The cylinder was heated for 22 hours at 250° . The product was taken off under reduced pressure at -76° , -36° , and room temperature.

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The first two fractions were passed over NaF pellets to remove HF. Infrared spectra of the samples revealed SOF₂, but not SF₄ or SF₆.

In other efforts to minimize the production of SOF_2 (i.e., to remove oxygen) the pulverized sulfur (5.152 grams) was allowed to soak in the 300 ml. stainless steel cylinder with 50 ml. of HF. After all volatiles were distilled off, the sulfur was pumped on for 12 hours. After that 26 ml. of HF and 8 ml. of Cl_2 were distilled in and the vessel heated at 200° for five hours. The IR spectra of the final fraction of the reaction product revealed a trace of SOF_2 and HC1.

Other reaction schemes intended to minimize the production of SOF_2 were tried. In one, 25 grams of sulfur were placed in a 300 ml. cylinder which was then evacuated for more than 24 hours. Then small amounts of Cl_2 and HF were added and the system heated to 200° for about 24 hours. The volatile products were removed and the procedure repeated three times. Each time the products were essentially SOF_2 and HCl. We had expected that the oxygen-containing species would be reacted out with the early reactions.

Flow systems were also tried. Three cylinders containing HF, Cl₂, and sulfur were tee'd into a section of $\frac{1}{2}$ copper tubing, 18 cm. of which was heated. The system was monitored by pressure gauges and temperature by two liquid nitrogen-cooled traps in parallel with each other. The heated section was brought to 375° . The sulfur recovered was maintained at 120° and and 760 torr of HF and 600 torr of Cl_2 were added to the system. The system was allowed to stand over the weekend in order to react out residual oxygen-containing species. The pressure dropped to 1/3 atmosphere. The volatile material was condensed into one of the cold traps. The oven temperature was brought to 525° and the sulfur reservoir to 214°. One atmosphere each of HF and Cl_2 was added. As the reaction proceeded the pressure dropped. After adding more HF and Cl₂, the heated section ruptured (probably predictably). The products were saved in the cooled trap. After replacement of the ruptured tubing the heated section temperature was kept at 300° and the experiment repeated. The products were condensed upon those frozen in the trap after the rupture. The products in the trap showed a trace of SOF2, SF4, and SF6, strong HCl bands, polymer and monomer bands of HF and an unidentified band at 700 cm. $^{-1}$. Other similar reactions where all of the tubing was Inconel gave strong SOF2 signals. Other schemes where sulfur and the other reactants were to diffuse into each other were tried without great success. Frequent plugging of valves was a problem wherever sulfur was to be transported in the vapor state.

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Selenium

A Monel cylinder containing 5.0 grams (.063 moles) of Se, 11.5 grams (.164 moles) of Cl₂ and 12.6 grams (.630 moles) of HF was heated for $15\frac{1}{2}$ hours at 250° . The cylinder was cooled to -34° , the volatiles removed, and the solid residue retained in the cylinder for elemental analysis. 100 ml. of solution prepared from 40 grams of NaOH pellets in 100 ml. of water was added to the reaction vessel (after the valve was removed) held at liquid nitrogen temperature. The valve was reattached and the cylinder evacuated while at liquid nitrogen temperature. The valve was closed and the cylinder and contents allowed to warm to room temperature overnight. In the morning the pressure within the cylinder was not in excess of that expected for an aqueous solution. Nickel and copper from the cylinder was precipitated with additional base and filtered off. Elemental analysis gave the ratio Se:Cl:F = 1.000:3.716:0.2385. Since the total halogen to selenium ratio was close to 4:1 there was a temptation to think in terms of a mixed halogen or a mixture of SeCl, and SeCl₂F. Further analysis, including analyses for Ni and Cu, showed a metal to selenium ratio of close to one and prompted efforts to determine if a complex was formed.

Chlorine was flowed through an 8 oz. Teflon bottle fitted with a $\frac{1}{2}$ " O.D. copper dip tube and exit tube adapted through a machined Teflon stopper adapter. The bottle contained 4.673 grams (.05918 moles) of metallic Se. After the Se was converted to SeCI₄, the dip tube assembly was warmed and the bottle filled about 2/3 full with anhydrous HF. The mixture boiled vigorously but there was no evidence of dissolution or reaction of the SeCI₄. The bottle was capped loosely in order to allow gases to escape. About 2/3 of the HF evaporated overnight. The bottle, without cap, was placed in a large vacuum dessicator containing CaSO₄ and NaF pellets. The dessicator was evacuated, isolated from the vacuum system, and kept under its own vapor pressure until no visible trace of HF was evident. Elemental analysis showed a mole ratio Se:Cl of 1.0:3.6. Only a trace of fluoride was present.

A horizontal 1 meter, $\frac{1}{2}$ " 0.D. Teflon tube containing 0.06127 moles of anhydrous NiF₂ and 0.06127 moles of metallic selenium was prepared. The end containing the NiF₂ was connected to a vacuum manifold while the other was attached to a source of dry Cl₂. The tube was evacuated and then Cl₂ passed through until the Se became SeCl₄. The Cl₂ was shut off and disconnected. The tube was tilted to an angle of 35⁰ and evacuated. Dry ice was packed around the tube and HF distilled in until the tube was about 2/3 full. The NiF₂ at the high end was slowly dropped in by gentle tapping on the tube. The pressure was only the vapor pressure of HF. There appeared to be no reaction. Overnight the pressure rose to about 1300 torr (total vapor pressure for HF and SeCl₄ should be 874 torr). There were no obvious changes in the appearance of the SeCl₄ or NiF₂. The contents of the tube were dumped into an 8 oz. Teflon bottle loosely capped where it could be shaken and HF added from time to time. There was a slow evolution of gas from the surface of the SeCl₄ over the period of two days while this was observed.

In order to determine the nature of the gas, 5 grams of SeCl_4 and 100 ml. of HF were placed in a 400 ml. Monel cylinder and allowed to stand for two days. A sample, at 200 torr, of the vapor phase was examined in the 500 cm.⁻¹ to 4000 cm.⁻¹ range. Three bands were observed: a weak HCl band, a strong HF polymer band, and an HF monomer band. A well-passivated 10 cm. Monel cell with AgCl windows was used. The average molecular weight of the gas was 36.94. A stainless steel cylinder containing 0.06330 moles of NaF₂, an excess of SeCl₄ (0.0633 moles), 50 ml. of HF and just enough Cl₂ to keep some Cl₂ in the cylinder was heated for 4 hours at 100°. The volatiles produced showed similar IR signals to the previous ones. The solid became contaminated with Se₂Cl₂ in handling.

A stainless steel cylinder containing 1.681 grams of anhydrous NiF_2 , an excess of freshly-prepared SeCl_4 (8 grams), 10 grams of HF, and 1 gram of Cl₂ was heated at 200° for 17 hours. The volatiles were removed at dry ice temperature. Nujol mulls on AgCl plates (one prepared with anhydrous NiF₂, the other with the solid from the reaction vessel) were prepared. The IR spectra from both showed the NiF stretching frequencies. There was no evidence of complexes.

Tungsten Trioxide

Stoichiometric amounts of WO_3 (.0430 mole), HF and Cl_2 (to give WF_6) were placed in a Monel cylinder and heated at 240° for 17 hours. Unfortunately, 1.4 grams weight loss occurred during heating. Infrared spectra of successive volatile fractions did not reveal any oxyhalides, water, or WF_6 . A number of unidentified bands were observed. The weight of the nonvolatile residue in the cylinder was within 0.8% of that expected for WOF_4 . An excess of HF and Cl_2 were condensed onto this residue and heated at 300° for 12 hours. The IR spectra of volatile samples showed no indication of oxyhalides, water, or WF_6 , but did show a surprisingly moderately strong signal for HCl. The non-volatile residue from this reaction was hydrolyzed

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in basic solvents and analyzed for chlorine (as AgCl), tungsten (as WO_3), and fluorine (modified Willard-Winter). The mole ratios were W:0:F = 1:2:2.

Other runs where the Parr Inconel bomb was used in connection with the gas chromatograph (column 20% Kcl-F oil on Kel-F powder -- the system passivated with a ClF_3 -HF mixture) were made. Excess of Cl_2 and HF and temperatures as high as 345° were used. No evidences of volatile tungsten fluoride were observed.

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REFERENCES

- 1 M. A. Gambardella, A. W. Jache and S. Kongpricha, U.S. Patent 3,446,592 (1969); A. W. Jache, S. Kongpricha and J. J. Pitts, U.S. Patent 3,451,775 (1969).
- 2 J. L. Russell and A. W. Jache, J. Inorg. Nucl. Chem. (in press).
- 3 J. J. Pitts and A. W. Jache, Inorg. Chem., 7, 1661 (1968).
- 4 B. Harvey and G. B. Porter, "Inorganic Physical Chemistry," Addison-Wesley Publishing Company, Reading Massachusetts, (1963), 404-412.
- 5 A. Glassner, U.S.A.E.C. Report ANL-5750 (1958).
- 6 O. E. Myers and A. P. Brady, J. Phys. Chem., <u>64</u>, 591 (1960).
- 7 J. L. Settle, H. M. Feder and W. N. Hubbard, J. Phys. Chem., <u>65</u>, 1337 (1961).
- 8 J. J. Katz and E. Rabinowitz, "The Chemistry of Uranium," Part I, Chapter 12, National Nuclear Energy Ser. Div., VII, 5 (1951).
- 9 M. H. Rand and O. Kubaschewski, "The Thermochemical Properties of Uranium Compounds," Interscience Publishers, New York, 13-25.

- 10 National Bureau of Standards Circular 500, U.S. Government Printing Office, Washington (1952).
- 11 J. Burgess, I. Haigh and R. D. Peacock, J. Chem. Soc. (Dalton), 1062 (1973).
- 12 A. F. Trotman, "Comprehensive Inorganic Chemistry," Dickenson, Pergamon Press, Vol. II, (1973) 856.
- 13 D. M. Yost and C. E. Kircher, J. Am. Chem. Soc., <u>52</u>, 4680 (1930).
- 14 H. Stammreich and R. Forneris, Spectrochim. Acta, 8, 46 (1956).
- 15 K. F. Zmbov, O. M. Uy and J. L. Margrave, J. Phys. Chem., 73, 3008 (1969).
- 16 JANAF, Thermochemical Tables, 2nd ed., D. R. Stull, et al., NSRDS-NBS-37, June, 1971.
- 17 V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold, London, (1966) 78, 130.
- 18 T. L. Cottrell, "The Strength of Chemical Bonds," 2nd ed., Butterworth, (1958).
- 19 K. Knox and C. E. Coffey, J. Am. Chem. Soc., 81, 5 (1959).
- 20 E. L. Muetterties and J. E. Castle, J. Chem. Soc., 3922 (1954).
- 21 J. G. Million, W. S. Pappas and C. W. Weber, J. of Chrom. Sci., <u>7</u>, 182 (1969); J. G. Million, C. W. Weber and P. R. Kuehn, AEC Research and Development Report K-1639.
- 22 J. Gaunt, Trans. Faraday Soc., <u>49</u>, 1122 (1953); T. G. Burke, J. Chem. Phys., <u>25</u>, 791 (1956).
- 23 C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, J. Am. Chem. Soc., <u>82</u>, 539 (1960).
- 24 C. Lau and J. Passman, J. Fluorine Chem., 6, 77 (1975).
- 25 K. F. Zmbov, O. M. Uy and J. L. Musgrave, J. Phys. Chem., 73, 3008 (1969)
- 26 B. Weinstock and G. L. Goodman, Advanc. Chem. Phys., 11, 169 (1965).
- 27 J. Gaunt, Trans. Faraday Soc., <u>49</u>, 1122 (1953); T. G. Burke, J. Chem. Phys., <u>25</u>, 791 (1956).
- 28 K. N. Tanner and A. B. F. Duncan, J. Amer. Chem. Soc., 73, 1164 (1951).
- 29 J. R. Geichman, E. A. Smith, S. S. Trond and P. R. Ogle, Inorg. Chem., <u>1</u>, 661 (1962).
- 30 D. Cook, S. J. Kuhn and G. A. Olah, J. Chem. Phys., 33, 1669 (1960).
- 31 J. Gaunt, Trans. Faraday Soc., <u>49</u>, 1122 (1953); T. G. Burke, J. Chem. Phys., <u>25</u>, 791 (1956).
- 32 T. G. Burke, D. F. Smith and A. H. Nielsen, J. Chem. Phys., <u>20</u>, 447 (1952).