A study on acid-base reactions of halides and oxide halides in anhydrous inorganic solvents

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OF HALIDES AND OXIDE HALIDES
IN ANHYDROUS INORGANIC SOLVENTS

1996

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YASUSHI KATAYAMA
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CHAPTER 1

General introduction

Some anhydrous inorganic solvents have unique characteristics as reaction media which enable chemical reactions not possible in aqueous or organic solutions to be performed for synthesizing novel compounds.

Anhydrous hydrogen fluoride (HF) is a volatile liquid at room temperature, the boiling and melting point being 19.51°C and −83.55°C, respectively[1]. It has a high dielectric constant, 83.6 at 0°C and 175 at −73°C[2], and is therefore a good solvent for ionic solutes. However, it must be used with caution because it is highly toxic and corrosive. The experiments in this study were carried out with a special equipment as described in Chapter 2.

Fluorine is a strong oxidizer to form a number of binary fluorides and oxide fluorides with high oxidation states, for example, Ag$^{III}$F$_3$[3], Ni$^{IV}$F$_4$, Ru$^{IV}$F$_4$, Os$^{IV}$F$_4$[4], Au$^{V}$F$_4$[5], Pt$^{VI}$F$_6$[6], Os$^{IV}$OF$_5$[7], Xe$^{VI}$F$_6$[8], Kr$^{VI}$F$_2$[9] and so on. These are stable in an inert atmosphere but easily react with reductive materials like moisture. Preparations and chemical reactions of such fluorides and oxide fluorides have been sometimes performed in HF because of its wide electrochemical window of −4.5V[2] which is suitable for studying such strong oxidizing species. The early works of acid-base reactions of several fluorides in HF were reported by Clifford et al.[10,11,12]. A number of complex salts of fluorides and oxide fluorides with unusual oxidation states have been prepared in HF[13]. The high oxidation states are stabilized in the form of complex anions coordinated by fluorine atoms in the compounds such as KAg$^{III}$F$_4$, CsCu$^{III}$F$_4$[13], KAg$^{III}$F$_4$[14], MAu$^{V}$F$_6$ (M = AgF, XeF$_{11}$, XeF$_5$, Cs, K, NO, O$_2$)[15,16], O$_2$Pt$^{VI}$F$_6$[17], Cs$_3$Nd$^{IV}$F$_7$, Cs$_3$Dy$^{IV}$F$_7$[13]. However, fundamental data, for example, the standard values of the enthalpy of formation of complex salts, the solubility in HF and the fluoride ion affinities of fluorides and oxide fluorides, especially of rare earth and actinide elements, are not
enough to elucidate acid-base reactions in HF.

LiCl-KCl eutectic system is also a good reaction media having a wide electrochemical window of 3.626 V[18] which makes it possible to prepare base metals such as alkaline, alkaline earth, rare earth metals and their intermetallic compounds. However, hygroscopic nature of these chlorides causes more or less contamination of oxide species which occasionally affect the electrochemical syntheses and measurements. It is important for practical use to clarify the chemical behavior of oxide ion in LiCl-KCl eutectic system.

In this study, acid-base reactions of some halides and oxide halides of rare earth elements, tungsten and uranium in HF (Chapter 3 to 7) and LiCl-KCl eutectic (Chapter 8) are focused from a viewpoint of fundamental research for syntheses of functional materials and reprocessing of spent nuclear fuels. Handling of some halides and oxide halides is not straightforward because of their hygroscopic natures. Chapter 2 describes techniques for handling and characterization of these materials without exposing to air. Moreover, safe handling of reactive gases and liquids are mentioned.

Chapter 3 describes reactions of silver (I and II) fluorides (AgF and AgF₂) and tungsten oxide tetrafluoride (WOF₄) in HF[19]. The physical and chemical properties of the compounds obtained by their reactions are also discussed.

In Chapter 4, reactions of silver(I) fluoride (AgF) and uranium hexafluoride (UF₆) are examined in HF[20], demonstrating the strong oxidizing ability of the latter. The unstable intermediate compound, argentus octafluorouranate (Ag₂UF₈), is discussed.

Chapters 5 and 6 deal with properties of uranyl fluoride (uranium dioxide difluoride, UO₂F₂) as a fluoroacid and fluorobase in HF[19]. In chapter 5, the property of UO₂F₂ in a basic HF solution of alkaline metal and silver(I) fluorides is discussed. The new complex oxofluorouranate (AgUO₂F₃) is characterized. In Chapter 6, the property of UO₂F₂ is focused on the reactions with strong fluoroacids in HF. The compounds of
uranyl fluoride and some pentafluorides are studied with the aids of X-ray powder diffraction and vibrational spectroscopy.

The properties of trivalent rare earth trifluorides as a fluoroacid and fluorobase in HF are investigated and described in Chapter 7[21]. The obtained compounds are characterized by X-ray diffraction and vibrational spectroscopy.

In Chapter 8, chemical behaviors of trivalent rare earth trichlorides in LiCl-KCl eutectic are discussed[22]. From the estimation of thermodynamic properties of rare earth oxide chlorides, the conditions of the formation of rare earth oxides and oxide chlorides are predicted and verified by experiments.
References


21 K. Hironaka, Y. Katayama, R. Hagiwara and Y. Ito, to be submitted to *J. Fluorine Chem.*

CHAPTER 2

Experimental techniques

2.1 Material handling

In general, most of materials used in this study must be handled in a glove box of argon atmosphere with a continuous gas refining instrument (Miwa Seisaku-sho, MDB-2BL-T1000+MS-H60W-O). The concentration of water was always monitored and maintained at less than 800 ppb (≈-100°C in a dew point). The concentration of oxygen was less than 500 ppb. This section describes the handling of reactive solids, gases and liquids without exposing them to air.

2.1.1 Solids

Hygroscopic materials must be dried under vacuum with elevating temperature. Drying was usually carried out in a Pyrex glass container (see 2.2.3). Drying over 500°C was made in a quartz glass container. The container was connected to a vacuum line constructed for vacuum drying (Fig. 2-1). Drying was usually performed by an oil diffusion pump until the pressure reaches 10^{-3} torr. After evacuating the gases, the container was heated to a fixed temperature in an electric furnace. Some special treatments were necessary for rare earth trichloride hydrates as described in Chapter 7. The container was then cooled and transferred in the glove box. The dried materials were stored in containers made of Pyrex glass, PFA (tetrafluoroethylene-perfluoralkylvinylether copolymer) or FEP (tetrafluoroethylene-hexafluoropropylene copolymer). Some highly oxidative materials were stored in FEP tubes (Sanyo, 1/2’ o.d.) with Teflon caps. Silver compounds were stored in containers covered with aluminum foil to avoid decomposition by the irradiation of light.
The air sensitive reagents were weighed by an electric balance (Shimadzu, EB-430H) settled in the glove box. The error was approximately ±3 mg due to the instability of the measurement caused by static electricity and circulation of gas in the glove box.

2.1.2 Gases

Gaseous materials were handled in a vacuum line constructed for corrosive gases such as fluorine, hydrogen fluoride and reactive fluorides. Fig. 2-2 shows a schematic illustration of the vacuum line. All the tubes and valves (Nupro, SS-8BK-TSW, Kel-F tip) used in the vacuum line are made of argon arc-welded stainless steel (SUS-316). The inner surface of the vacuum line was pre-passivated with fluorine gas (~1 atm) for 10 ~ 20 hours at room temperature. The pressure was monitored by Bourdon and Pirani gauges. The latter must not be exposed to reactive gases filled in the line. The volumes of each part of the line were tensimetrically measured prior to the experiment.

The reactive gases were disposed through a series of chemical trap columns, a sodium fluoride (NaF) column for trapping gaseous fluoroacids and a soda lime column.
Fig. 2-2 Vacuum line for handling of fluorine, hydrogen fluoride and fluoride gases.
for trapping fluorine and other fluoroacids passed through the NaF column, the reactions in the traps being represented as follows:

\[
\begin{align*}
MF_n + mNaF & \rightarrow Na_mMF_{m+n} \\
F_2 + CaO & \rightarrow CaF_2 + 1/2 O_2 
\end{align*}
\]

Pumping of the chemical traps was performed through a cold trap.

The amount of gases for reactions was measured by tensimetry. In some cases, the gases were introduced in reactors by condensation. Fluorine gas, for example, is a liquid with vapor pressure of -0.4 atm at liquid nitrogen temperature (-176°C). It should be noted that wrong handling in condensation process may cause serious accidents like a pressure explosion of a reactor when it is warmed up. It is necessary to calculate precisely the amount and pressure of gases to be condensed in a reactor. A high pressure reaction needs the protection against explosion such as protection glasses and a thick plastic shield in front of the reactor.

The impurities in the gases were checked by infrared absorption spectroscopy using a gas cell with AgCl crystal windows (See 2.7.2). Gaseous fluorides prepared by the reactions of metals or metal oxides with fluorine were purified by a trap-to-trap distillation.

2.1.3 Liquids

Liquid materials used at room temperature in this study were HF (m.p. -83.1°C, b.p. 19.54°C[1]), WF₆ (m.p. 2.5°C, b.p. 17.5°C[1]), SbF₅ (m.p. 7°C, b.p. 149.5°C[1]) and acetonitrile (CH₃CN, m.p. -45.7°C, b.p. 81.6°C[1]). At high temperature, LiCl-KCl eutectic (LiCl : KCl = 58.5 : 41.5 in mol%, m.p. 354°C) was employed as a solvent.

HF is a colorless liquid and the vapor pressure is ~1.3 atm[2] at room temperature. It was stored in a container made of Kel-F tube to avoid formation of hydrogen by the reactions with metals. A small amount of HF was transferred to an FEP container (3/4' o.d.) in which a strong oxidizer, K₂NiF₆ (Ozark-Mahoning), was placed in order to
eliminate reducing materials, such as water and hydrogen. HF was distilled from the $K_2NiF_6$ solution to a reactor cooled at $-196^\circ C$.

Vapor pressure of $WF_6$ at room temperature is also ~1.3 atm[2]. Therefore, the handling is similar to that of HF. However, a Kel-F container must be used for storage
since $WF_6$ penetrates FEP wall.

$SbF_3$ is a colorless viscous liquid with a low vapor pressure (~4 torr at 25°C[2]). Liquid $SbF_3$ was handled in the glove box. A special apparatus was used to transfer $SbF_3$ in the vacuum line (Fig. 2-3). $SbF_3$ was condensed on the cooled surface of outer tube applying a dynamic vacuum through an inner FEP tube.

LiCl-KCl powder mixture was loaded in a Pyrex glass reactor in the glove box and it was connected to the manifold line in order to keep argon atmosphere over the melts. The salts were heated by a transparent electric furnace (see 2.3) monitoring the melting and precipitation of compounds. The temperature of the melts was monitored by a thermocouple attached to the bottom of the reactor.

The volume of a liquid in a cylindrical reactor was estimated from the inner diameter and the height of the liquid-level from the bottom of the reactor.

2.2 Reactors

2.2.1 FEP Reactors

FEP reactors were used for the reactions performed in liquid HF at room temperature (Fig. 2-4). The one end of an FEP tube (10 mm, 1/2 or 3/4" o.d., 150 ~ 200 mm long) was heat-sealed pressing by pliers. The other end was connected to a stainless steel valve (Whitey, SS-1KS4, with Kel-F tips) via a reducing union with Swagelok Teflon fittings. The maximum working pressure and temperature were less than ~3 atm and ~120°C, respectively.

T-shaped FEP reactors were occasionally used for decantation to separate a solid from liquid, or wash a solid with HF. Fig. 2-5 shows a T-shaped FEP reactor. Two FEP tubes (10 mm or 1/2" o.d.) with a sealed end are connected to Teflon T-union (Sanyo) with compression fittings so that the liquid does not contact with metal by decantation.

The stirring of the liquid in the FEP tube was carried out by snapping it with fingers
or magnetically spinning a small magnet coated with Teflon in the reactor.

### 2.2.2 Monel reactors

Monel (an alloy of nickel and copper) reactors were used when reactions of corrosive gases were performed at high temperature and/or high pressure. Figure 2-6 shows a typical Monel reactor. All the parts contacting with gases are made of argon arc-welded Monel metal. A Teflon packing was used to seal between the body and lid. The lid was cooled by a water flow through a jacket to protect the Teflon packing. The reactor was passivated with fluorine for several hours at room temperature before use. The maximum temperature and pressure for reactions in the presence of fluorine were ~ 500°C and ~ 12 atm, respectively. Samples were usually put on nickel foil cups. The Monel reactor was heated by a ribbon heater wound around it. The temperature was monitored.
by a thermocouple attached on the outer surface near the bottom of the reactor.

When the product is sublimable, it deposits on the inner surface of the lid. Pure tungsten oxide tetrafluoride and bismuth pentafluoride were collected without further purification (see Appendix).

2.2.3 Pyrex and quartz glass reactors

Pyrex and quartz glass reactors were used for vacuum drying of the reagents and the reactions performed at higher temperatures including LiCl-KCl molten salts. A Pyrex glass reactor is illustrated in Fig. 2-7. The tube was connected to a stainless steel valve via Swagelok fitting with Teflon ferrule. The temperature was maintained lower than ~500°C. When a higher temperature was required, quartz glass reactors were used.

A large quartz glass reactor (25 mm o.d.) with a joint was used for drying a large amount of solid reagents and capillaries for X-ray powder diffraction and Raman spectroscopy (Fig. 2-8).
2.2.4 Sublimation apparatus

Some reagents were purified by sublimation. Fig. 2-9 shows a sublimation apparatus made of Pyrex glass. A Byton o-ring was used to seal between the vessel and lid. A crude material was placed at the bottom of the vessel. The vessel was then warmed up under reduced pressure while the cold finger to collect the sublimed material was cooled by a water flow.

2.3 Transparent electric furnace

Fig. 2-10 shows a transparent electric furnace made of quartz glass. A nichrome wire was wound around the inner quartz glass tube. The outer tube was placed for heat insulation. The tubes were flexibly held with spring screws to protect from break by heat expansion. A thermocouple covered with an alumina tube was inserted in a brass holder at the center of the bottom. A reactor was inserted from the top and fixed so that the bottom touches on the top of the thermocouple.
2.4 Experimental techniques

2.4.1 Experimental technique for handling anhydrous hydrogen fluoride

Solid reagents were loaded in an FEP reactor in the glove box. The reactor was connected to the vacuum line via Swagelok fitting with Teflon ferrule. The gases in the reactor was evacuated after evacuating air in the connecting part between the reactor and the vacuum line. HF was distilled from a solution of $\text{K}_2\text{NiF}_6$ to the reactor. The amount of HF transferred was estimated by the liquid-level of the $\text{K}_2\text{NiF}_6$ solution. The reactor was warmed up slowly to room temperature. The reaction was continued for 2-20 hours with/without stirring. HF was evacuated slowly from the reactor after the reaction. Occasionally, the evacuation rate was controlled by a needle valve (Nupro, SS-4BMG) placed between the reactor and the vacuum line. The reactor was then transferred into the
glove box. The product was charged in a quartz glass capillary to prepare the sample for X-ray powder diffraction and Raman spectroscopy.

Single crystal growth was carried out in a T-shaped FEP reactor. A sample or mixture of reagents was loaded in one arm (Tube A) of the reactor and HF was condensed on it. The supernatant solution was decanted to another arm (Tube B). Then, HF in Tube B was condensed slowly back to Tube A cooled by water. Slow elimination of HF controlled by a needle valve was also successful in single crystal growth. In most cases, single crystal growth takes several days.

2.4.2 Experimental technique for handling molten chlorides

Reagents were mixed with LiCl-KCl eutectic mixture and loaded in a Pyrex glass reactor. Ambient pressure of Ar was kept in the reactor. The temperature was elevated to 450°C by the transparent electric furnace to monitor melting of the mixture and formation of precipitate. After holding the temperature for several hours, the reactor was cooled slowly and transferred to the glove box. The precipitate was collected from the cooled melts and charged in a quartz glass capillary to prepare the sample for X-ray powder diffraction as described in the next section.

2.5 X-ray powder diffraction

X-ray powder diffraction patterns were obtained by a Debye-Scherrer camera of 11.5-mm in diameter with Rigaku apparatus using CuKα radiation (Ni-filtered). Samples were usually packed in 0.3 or 0.5 mm o.d. quartz glass capillaries (Overseas X-ray) in the glove box. The capillaries were temporarily sealed by grease and transferred outside of the glove box. Then they were sealed by drawing down in a small flame of an oxygen burner.

The d-spacing of X-ray powder diffraction patterns was usually measured by a
comparator (Shimadzu). The patterns were occasionally transferred to a personal computer with the aid of a scanner to measure the intensities of diffraction peaks although they are not rigorously proportional to the real intensities. There is a tendency that the transmittance saturates as the intensity of a peak increases. Recently, imaging plates were introduced for the measurement of X-ray powder diffraction patterns instead of films giving proportional intensities of the diffraction.

2.6 Raman spectroscopy of solid samples

The Raman spectra of the solid samples were obtained by NR-1000S (Nippon Spectroscopic), 512.5 and 488 nm lines of Ar laser (NEC), or 647.1 nm line of Kr laser (Spectra Physics) being used as excitation lines. The samples were loaded in 0.5 or 1.0 mm o.d. quartz glass capillaries in the same way as for the samples of X-ray powder diffraction. The Raman scattering light was introduced to the spectrometer from the direction perpendicular to the excitation beam. Colored samples should be irradiated by laser as shortly as possible otherwise the absorption of light causes decomposition. This may be avoided by changing the wavelength and/or power of the laser.

2.7 IR Spectroscopy

2.7.1 Solid samples

A finely grounded powder of a solid sample was sandwiched between two AgCl crystal windows in an air-tight solid cell (Fig. 2-11). The surfaces of AgCl windows were scratched by a sand paper to avoid interference. The spectrum of the sample was measured on FTIR spectrometers (FT/IR-5M, Nippon Spectroscopic or BIORAD FTS 165).
2.7.2 Gaseous samples

Gaseous sample (50–100 torr) was introduced in a gas cell with AgCl crystal windows (Fig. 2-12). A cold finger is equipped to collect gases by condensation. The spectra were recorded using an FTIR spectrometer (BIORAD FTS 165).

Fig. 2-11 IR cell for solid samples.

Fig. 2-12 IR cell for gaseous samples.
References


CHAPTER 3

Reactions of silver(I,II) fluorides with tungsten oxide tetrafluoride in anhydrous hydrogen fluoride

3.1 Introduction

Silver fluoride (AgF) acts as a strong fluorobase in anhydrous hydrogen fluoride (HF) like alkaline metal fluorides dissolving well in HF (83.2 g/100 g HF at 11.9°C[1]). Complex salts of AgF have been prepared by the reactions with several fluoroacids[2] although only a few crystal structures have been known due to low solubility in HF which prevents growth of single crystals.

On the other hand, silver difluoride (AgF₂) is a very weak fluorobase and reacts only with strong fluoroacids. It reacts with antimony and bismuth pentfluoride (SbF₅ and BiF₃) to form Ag(SbF₅)₂ and Ag(BiF₃)₂, respectively[3]. These compounds contain discrete divalent silver cations, Ag²⁺. The reactions with arsenic pentafluoride (AsF₅) and boron trifluoride (BF₃) give 1:1 complex salts, AgFAsF₆ and AgFBF₄, respectively[4,5]. These 1:1 compounds contain one-dimensional polymeric cationic chains, (AgF)n⁺, which is considered to be decomposed to monomeric Ag(II) cations in the solution acidified by AsF₅ and BF₃.

Tungsten oxide tetrafluoride (WO₄²⁻) has been known to act as a fluoroacid to form several complex salts, such as NaWO₄, CsWO₄[6], NOWO₄[7], CsW₂O₇F₉[8] and XeF₂WO₄[9]. The fluoride ion affinity of WO₄²⁻ is known to be fairly strong although quantitative assessment is lacking.

In this chapter, WO₄²⁻ as a fluoroacid in HF is examined through the series of reactions with AgF and AgF₂. Some chemical and physical properties of the complex salts

will be discussed.

3.2 Reagents

Xe (Teisan K. K., purity 99.995% or more) was used as supplied. AgF was prepared by interacting Ag₂O (Wako Chemicals, purity 99% or more) with HF. Decomposition of the bifluoride, Ag(HF)ₙF, was made at 80°C under vacuum. AgF₂ was prepared by fluorinating AgNO₃ (Nakarai Tesque, purity 99.95%) in a Monel reactor at 250°C. WOF₄ was prepared by the reaction of WF₅ (Ozark-Mahoning) with water formed by a slow reaction of quartz wool (Toshiba) and HF[10]. Purification was made by sublimation at ~70°C under a reduced pressure.

3.3 Results

\[ AgF + 2WOF_4 \]

AgF (50 mg, 0.394 mmol) and WOF₄ (225 mg, 0.816 mmol) were interacted for several hours in HF (~1 cm³) at room temperature. After removing HF, an ivory solid was obtained. No weight change was observed after the reaction. X-ray diffraction showed the absence of the starting materials. The solid was ascribed to the 1 : 2 complex salt, Ag₆W₂O₂F₉, by the comparison of the vibrational spectra of the solid with those of Cs₆W₂O₂F₉[8].

\[ AgF + WOF_4 \]

The mixture of AgF (123 mg, 0.962 mmol) and WOF₄ (266 mg, 0.964 mmol) was loaded into one arm (Tube A) of a T-shaped reactor and HF (~1 cm³) was condensed on the mixture at ~196°C. An ivory precipitate was formed after warming Tube A to room temperature. The supernatant solution was decanted to the other arm (Tube B) and the
precipitate was washed several times with HF condensed back to Tube A. Finally, after evaporating HF, an ivory solid (~270 mg) in Tube A and a colorless solid in Tube B were obtained. Additional evacuation with warming of Tube B changed the color of the solid to bright yellow (the weight: ~80 mg). A large weight loss (~40 mg, probably caused by sticking of the sample in the T-union) prevented the determination of the composition by gravimetry. X-ray diffraction showed that the yellow solid was AgF and the ivory solid was the same as obtained by the interaction of AgF + 2WOF₄.

\[ \text{AgF} + \text{WOF}_4 \text{ (slow evacuation of HF)} \]

AgF (107 mg, 0.843 mmol) and WOF₄ (227 mg, 0.823 mmol) were loaded in one arm (Tube A) of a T-shaped reactor and HF (~1 cm³) was condensed on the mixture at -196°C. An ivory solid was formed as described above. On removing HF very slowly by condensing in the end of the other arm cooled at 0°C, a colorless crystalline solid was formed in Tube A. No weight uptake was observed after the reaction. X-ray diffraction detected neither AgF nor WOF₄. The solid is ascribed to the 1:1 complex salt, AgWOF₅, by comparing the vibrational spectra with those of NOWOF₃[7].

\[ \text{AgF}_2 + 2\text{WOF}_4 \]

AgF₂ (168 mg, 1.15 mmol) and WOF₄ (640 mg, 2.32 mmol) were interacted in HF (~2 cm³) in the presence of F₂ at room temperature. After stirring for ~24 hours, a dark-purple solid was obtained. No weight change was observed after the reaction. No phases of the starting materials were observed in the X-ray powder pattern. The solid is considered to be the 1:2 complex salt, AgFW₂O₂F₉, from the comparison of the vibrational spectra with those of AgW₂O₂F₉ which contains W₂O₂F₉⁻ anion.

\[ \text{AgF}_2 + \text{WOF}_4 \]

AgF₂ (103 mg, 0.706 mmol) and WOF₄ (187 mg, 0.678 mmol) were interacted in
HF (~2 cm³) in the presence of F₂ at room temperature. On evacuating HF very slowly, a dark-purple solid was obtained. No weight change was observed after the reaction. This solid was ascribed to the mixture of AgFW₂O₂F₉ and unreacted AgF₂ by X-ray diffraction.

\[ \text{AgFW}_2\text{O}_2\text{F}_9 + \text{F}_2 \]

AgFW₂O₂F₉, which was prepared above, was interacted with F₂ in HF (~1 cm³) at room temperature. The color of the precipitate (ivory) turned to brown after stirring for a while. Additional interaction for 24 hours changed the color of the precipitate to dark-purple. X-ray diffraction of the precipitate detected AgFW₂O₂F₉ and AgF₂.

\[ \text{AgFW}_2\text{O}_2\text{F}_9 + \text{Xe} \]

AgFW₂O₂F₉ prepared above was interacted with Xe in HF (~1 cm³) at room temperature. In ~24 hours, the color of the precipitate changed gradually from dark-purple to brown. After evacuating HF at room temperature, a sublimable and highly reactive colorless solid was crystallized at the upper part of the reaction tube by warming the bottom of it. The solid was identified as XeF₂.WOF₄[9] by Raman spectroscopy. X-ray diffraction showed that the residual solid in the bottom of the tube was the mixture of AgF₂ and AgFW₂O₂F₉.

3.4 Discussion

It is known that WOF₄ dissolves to form a monomeric anion, WOF₅⁻, and a dimeric anion, W₂O₂F₉⁻ in HF, by the following equilibria[7]:

\[ 2\text{HF} + \text{WO}_4^- = \text{H}_2\text{F}^+ + \text{WO}_5^- \] (1)

\[ n\text{HF} + 2\text{WO}_5^- = \text{W}_2\text{O}_2\text{F}_9^- + (\text{HF})_n\text{F}^- \] (2)

According to these equilibria, the 1 : 2 complex salt of AgF and WOF₄, AgFW₂O₂F₉, is
formed in the presence of excess HF. The 1 : 1 complex salt, AgWOF₅, is formed by slow removal of HF, in other words, by shifting the following equilibrium to the left:

\[ 2\text{AgWOF}_5 + n\text{HF} \rightarrow \text{Ag(HF)}_n\text{F} + \text{AgW}_2\text{O}_2\text{F}_9 \]  

AgW₂O₂F₉ is also prepared by interacting stoichiometric amounts of AgF and WOF₄ in HF:

\[ \text{AgF} + 2\text{WOF}_4 \rightarrow \text{AgW}_2\text{O}_2\text{F}_9 \]  

The X-ray powder patterns of AgWOF₅ and AgW₂O₂F₉ are listed in Table 3-1. Table 3-2 shows the vibrational spectra. The spectra of NOWOF₅[7] and CsW₂O₂F₉[8] are also included for comparison. The peaks for WOF₃⁻ are assigned for C₄v symmetry[11]. The spectra of AgWOF₅ and AgW₂O₂F₉ are quite similar to those of NOWOF₅ and CsW₂O₂F₉, respectively.

Table 3-1 X-ray powder diffraction patterns of AgWOF₅, AgW₂O₂F₉, and AgFW₂O₂F₉.

<table>
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<tr>
<th>AgWOF₅</th>
<th>AgW₂O₂F₉</th>
<th>AgFW₂O₂F₉</th>
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Abbreviations used: s, strong; m, medium; v, very; w, weak.

*a_0 = 10.402, b_0 = 12.307, c_0 = 13.639 Å, β = 90.2°; space group, P2_/c[12].

25
Table 3-2  Vibrational spectra of solid AgWOF₅, AgW₂O₂F₉, AgFW₂O₂F₉ and some related compounds.

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<th>AgFW₂O₂F₉</th>
<th>NOWOF b</th>
<th>CsW₃OF₉ c</th>
<th>Assignments</th>
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<td>IR</td>
<td>Raman</td>
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<tr>
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<td>1026s</td>
<td>1009s,br</td>
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<td></td>
<td></td>
<td></td>
<td>v(W=O in phase)</td>
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<tr>
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<td>645s,br</td>
<td>645s,br</td>
<td>610vs,br</td>
<td>610vw</td>
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<td>610w</td>
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<td>615ms</td>
<td>602s,br</td>
<td>591vw</td>
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<td>440w</td>
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<td>330s</td>
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<td>v₉(E), π(W-F₄)</td>
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<td>v₄(A¹), π(W-F₄)</td>
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</table>

*Frequencies are given in cm⁻¹. Abbreviations used: sh, sharp; br, broad; s, strong; m, medium; v, very; w, weak. bThe spectra reported in ref. 7. The peaks corresponding to N-O are not listed. cRef. 8. dRef. 11.
It has been reported that AgF$_2$ reacts with strong fluoroacids to give cationic Ag(II), (AgF)$_n$$^{n+}$ and/or Ag$^{2+}$[4,5,13,14]. Two isomers, AgF$^+$$W_2O_2F_9^-$ and Ag$^{2+}$(WOF$_5^-$)$_2$, are possible for the 1 : 2 compound of AgF$_2$ and WOF$_4$. The vibrational spectra of this compound are listed in Table 3-2. It is evident that this compound contains W$_2O_2F_9^-$ by comparing the spectra with those of AgWO$_5$ and AgW$_2$O$_2$F$_9$. The powerful oxidizing ability discussed below indicates that this compound contains (AgF)$_n$$^{n+}$. Therefore this compound is concluded to be AgFW$_2$O$_2$F$_9$. The X-ray powder pattern is listed in Table 3-1.

AgFW$_2$O$_2$F$_9$ is stable under an inert gas but irradiation of this compound sealed in a quartz glass capillary by Ar laser (488 and 514.5 nm, 50-250 mW) causes decomposition probably to AgW$_2$O$_2$F$_9$ and fluorine, the latter seems to have etched the quartz wall. The Raman spectrum was obtained by using a Kr laser (647.1 nm, 50 mW) beam which does not cause decomposition (Table 3-2).

Interaction of equimolar amounts of AgF$_2$ and WOF$_4$ does not form the 1 : 1 complex salts such as AgFWOF$_5$, but gives a mixture of AgFW$_2$O$_2$F$_9$ and unreacted AgF$_2$. WOF$_4$ is considered to act as a stronger fluoroacid by forming W$_2$O$_2$F$_9^-$ rather than forming WOF$_5^-$, the latter being unable to form an (AgF)$_n$$^{n+}$ salt.

Ag$^+$ is oxidized by F$_2$ to form cationic Ag(II) such as Ag$^{2+}$ and (AgF)$_n$$^{n+}$ in the presence of SbF$_5$, AsF$_5$ and BF$_3$[5,13]. The formation of AgF$^+$$W_2O_2F_9^-$ by the reaction of AgW$_2$O$_2$F$_9$ with F$_2$ demonstrates that the fluoroacidity of WOF$_4$ by forming W$_2$O$_2$F$_9^-$ is at least as strong as that of BF$_3$.

\[ AgW_2O_2F_9 + 1/2F_2 \rightarrow AgFW_2O_2F_9 \] (5)

The formation of AgF$_2$ (brown) is observed at the beginning of the reaction. Ag$^+$ is oxidized to Ag(II) by F$_2$ in the presence of a trace amount of WOF$_4$, formed according to the equilibria expressed by eqs. (1) and (2). However, AgF$_2$ would precipitate instead of AgFW$_2$O$_2$F$_9$ when the solution is not acidic enough due to the low solubility of AgW$_2$O$_2$F$_9$ in HF. Since the reaction rate of AgF$_2$ and WOF$_4$ is slow, because the former
is insoluble again, AgFW_2O_2F_9 is formed very slowly as the fluoroacidity is increased by the precipitation of AgF_2.

According to the crystal structure of H_3O+W_2O_2F_9^- [15], W_2O_2F_9^- consists of two WOF_4 units linked by a fluorine bridge trans to the tungsten-oxygen bonds. At the same time as this work was carried out, Shen et al. also performed a series of reactions of AgF and AgF_2 with WOF_4 [12]. They succeeded in growing a single crystal of AgW_2O_2F_9 and determined the crystal structure, in which they found two types of fluorine-bridged dimeric anions, slightly different in bond angles and conformation with each other. The assignment of the powder pattern of AgW_2O_2F_9 in Table 3-1 was made based on their result.

Xe is oxidized to Xe(II) by cationic Ag(II) in HF at room temperature [13]. AgFW_2O_2F_9 also oxidizes Xe to Xe(II) by the following reaction in HF:

\[ 5AgFW_2O_2F_9 + 2Xe \rightarrow 2XeF_2WOF_4 + 4AgW_2O_2F_9 + AgF_2 \]  

Since the fluorobasicity of XeF_2 is stronger than that of AgF_2, XeF_2 substitutes AgF_2 in AgFW_2O_2F_9 to form XeF_2WOF_4. All Ag(II) is not consumed for the oxidation of Xe to Xe(II) due to the precipitation of AgF_2 which does not oxidize Xe unless further WOF_4 is added to the solution.
References

CHAPTER 4

Reaction of silver fluoride and uranium hexafluoride
in anhydrous hydrogen fluoride

4.1 Introduction

Uranium hexafluoride is expected to be a powerful fluorinating agent if one notes the first U-F bond dissociation energy (143 kJ mol⁻¹[1]) is lower than F-F bond energy. In fact, UF₆ fluorinates SO₂ in gas phase to give S₂O₅F₂ like F₂ and XeF₂[2], which is a good example of the fluorination power of it.

For the fluorination reaction in solution, water is not a suitable solvent because UF₆ reacts with it to give UO₂F₂. The highest oxidation state of uranium, 6+, is stable in the form of uranyl ion, UO₂²⁺, in aqueous solution. Liquid anhydrous hydrogen fluoride (HF) is one of the best candidates as solvents since it is stable against strong oxidizers, and one can avoid formation of stable uranyl ions. This chapter demonstrates the oxidizing power of UF₆ in HF which is able to fluorinate the cationic Ag(I) to Ag(II) at ambient temperature and clarify the reaction mechanism.

4.2 Reagents

AgF was prepared as described in Chapter 3. UF₆ was prepared by fluorinating UO₂ (Furukawa Denki Kogyo, depleted uranium) in a nickel metal reaction vessel at around 500°C, and distilled into a Monel metal container after evacuating volatile gases at 0°C for a while. UF₆ (β-form) was prepared by irradiating UV light of a mercury lamp (Hitachi UM-102) on a gaseous mixture of UF₆ and carbon monoxide (Takachiho

Kagaku Kogyo, spectroscopic grade) in a Pyrex glass bulb. AgFBF$_4$ was prepared by fluorinating AgBF$_4$ prepared by the interaction of AgF and BF$_3$ in liquid hydrogen fluoride[3]. Hydrogen fluoride (Daikin Kogyo, purity 99 % or more) was dried over K$_2$NiF$_6$ (Ozark-Mahoning) to remove trace amount of water. Fluorine (Daikin Kogyo, purity, 99.7 %) and xenon (Teisan K. K., purity 99.995 % or more) were used as supplied. No impurities were detected by IR spectroscopy in the gaseous samples (~200 mm Hg) transferred to a gas cell with silver chloride windows. The purity of the solid materials was checked by X-ray powder diffraction.

4.3 Results

\[ AgF + UF_6 \text{ in HF (interacted overnight)} \]

UF$_6$ (>10 mmol) was condensed over AgF (4.54 mmol) with HF (~4 cm$^3$) in an FEP tube at -196°C. At room temperature, a saturated colorless solution was formed with a colorless precipitate of UF$_6$ at the bottom of the reaction tube. After starting agitation of the solution with a stirring bar for a few minutes, a red solid gradually precipitated from the solution. The color of the precipitate slowly turned dark brown. The bubbling almost ceased after overnight reaction. Volatile materials in the tube were all condensable at -196°C. The weight uptake of the product indicates that 2 moles of AgF reacts with 1 mole of UF$_6$. Elemental analyses of Ag and U of the product agreed with this result (obsd., Ag: 36.4, U: 39.4, F (the rest): 24.2 wt%, calcd., Ag: 35.6, U: 39.3, F: 25.1 wt%). The X-ray powder diffraction detected a cubic phase ($a_0 = 8.513$ Å, see Table 4-1) in addition to AgF$_2$[4] and AgUF$_6$[5] in the product.

\[ AgF + UF_6 \text{ in HF (interacted for 20 minutes)} \]

In the one end of a T-shaped FEP tube (Tube A), AgF (1.48 mmol) dissolved in HF (~2 cm$^3$) was interacted with UF$_6$ (2.7 mmol) to give a colorless solution. After
starting the agitation of the solution with a stirring bar for a few minutes, a red solid gradually precipitated from the solution. After 20 minutes of stirring, the solution was decanted to the side tube (Tube B). From the solution in Tube B, a white solid precipitated which gradually turned yellow by evacuation. All the lines in the X-ray diffraction powder pattern of the precipitate in Tube A were ascribed to those of AgF[6], AgF$_2$[4], AgUF$_6$[5] and the cubic phase identified above. Only AgF was detected from the powder pattern of the yellow solid remained in Tube B.

\[ \text{Xe} + \text{AgF} + \text{UF}_6 \text{ in HF} \]

AgF (4.8 mmol) and UF$_6$ (7.3 mmol) were condensed with HF (4 cm$^3$) to prepare a saturated solution. Xenon gas was introduced in the tube (the total pressure was around 1.4 atm at room temperature). A red solid gradually precipitated from the solution as in the case of the reaction without xenon. The color of the precipitate changed to dark brown after overnight reaction. The solution was always stirred during the reaction. A week later, the volatile materials (the total pressure was unchanged from the beginning of the reaction) were evacuated at 0°C after sampling a part of it for IR measurement. X-ray powder diffraction detected only AgF$_2$[4] and AgUF$_6$[5] in this solid. Only HF and UF$_6$ were observed in IR spectra of the volatile materials. From the weight uptake, the Ag / U ratio of the residual solid was two, the same as in the case without supplying xenon.

\[ \text{AgFBF}_4 + \text{UF}_5 \text{ (\beta-form) in HF} \]

AgFBF$_4$ (0.913 mmol) was interacted with \( \beta \)-UF$_5$ (0.901 mmol) in liquid HF (2 cm$^3$) at room temperature. A gas evolution was observed during the reaction. IR spectroscopy detected UF$_6$ from the volatiles. A significant weight loss (302 mg, 0.86 mmol, assuming only UF$_6$ was released) was observed after evacuation. X-ray powder diffraction of the residual solid detected AgBF$_4$[7] and unreacted \( \beta \)-UF$_5$[8].
Decomposition of the reaction product

The reaction product of AgF + UF₆ sealed in a quartz glass capillary in which the cubic phase was detected by X-ray diffraction was kept at room temperature over a month. In the X-ray diffraction powder pattern, the cubic phase disappeared and only the AgF₂[4] and AgUF₆[5] were observed. No evolution of UF₆ was confirmed on the same sample of a large quantity kept in a sealed Pyrex glass ample. UF₆ was not collected by cooling the one end of the tube at liquid nitrogen temperature. About 1 g of the sample was put in water (2 cm³) in a FEP test tube. A gas evolution occurred from the green solution formed.

4.4 Discussion

The ionization potential of Ag⁺(g) (21.49 eV[3]) is the highest of all the singly charged metal cations except alkaline metals. Fluorinations of AgF by strong fluorinating agents such as F₂[9], XeF₂[10], ClF₃[10] and BrF₃[11], using HF or themselves as solvents, all failed at ambient temperature. The calculated free enthalpy changes of these reactions are large negative values[12]. The failure of the reactions should have some kinetic reasons. A possible explanation is that these fluorinating agents are all strong electrophiles and cannot effectively attack cations in solution.

In HF, 2 moles of AgF reacts with 1 mole of UF₆ as follows.

\[ 2\text{AgF} + \text{UF}_6 \rightarrow \text{AgF}_2 + \text{AgUF}_6 \]  

The free enthalpy change of this reaction has been calculated to be \(-67 \pm 15 \text{ kJ mol}^{-1}\)[12]. When UF₆ is interacted with HF solution saturated with AgF, a red solid precipitates in the beginning which gradually turns dark brown. Although the formation of AgF₂ was denied in the earlier work[10], we confirmed the existence in the product of every run in experiments by X-ray powder diffraction (Table 4-1).
Table 4-1 X-ray powder data for the reaction product of AgF and UF₆.

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<th>10^4d² Å^-2 (calc.)</th>
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<th>10^4d² Å^-2 (calc.)</th>
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</table>

AgUF₆: \(a₀ = 5.4491(8)\) Å; space group, \(P4_2/mcm\)[5].
AgF₂: \(a₀ = 5.813, b₀ = 5.529, c₀ = 5.073\) Å; space group, \(Pbc\alpha\)[4].
Ag₂UF₈: \(a₀ = 8.513\) Å, cubic.
When the reaction product is interacted with water, oxygen evolution and
disproportionation of the U(V) to U(VI) and U(IV) are observed.

\[ 4\text{AgF}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ag}^+ + 4\text{H}^+ + 8\text{F}^- + \text{O}_2 \uparrow \]  
(2)

\[ 2\text{AgUF}_6 + 2\text{H}_2\text{O} \rightarrow 2\text{Ag}^+ + \text{UO}_2^{2+} + \text{UF}_4 + 4\text{H}^+ + 8\text{F}^- \]  
(3)

In addition to AgF₂ and AgUF₆, a cubic phase \((a_0 = 8.513 \text{ Å})\) exists in the reaction
product as shown in Table 4-1. This phase disappears slowly from the reaction product
kept in a sealed quartz glass tube.

The solubility of UF₆ in HF is about 0.5 M and Raman bands of UF₆ in the
solution are almost unchanged from those of pure material[13], suggesting that the
following equilibria[14] shift to the left side.

\[ 3\text{HF} \leftrightarrow \text{H}_2\text{F}^+ + \text{HF}_2^- \]  
(4)

\[ \text{UF}_6 + \text{HF}_2^- \leftrightarrow \text{UF}_7^- + \text{HF} \]  
(5)

When a fluorobase is dissolved in HF, the concentration of bifluoride ion is increased
according to the following equilibrium.

\[ \text{M}^+ + \text{HF} \leftrightarrow \text{M}^0 + \text{HF}_2^- \]  
(6)

Therefore the concentration of UF₇⁻ is also increased according to eq. 5. In the present
study, the solubility of UF₆ is remarkably increased by dissolving AgF which acts as a
fluorobase in HF. It has been reported that UF₈²⁻ ion is also formed in the basic
condition[14].

\[ \text{UF}_7^- + \text{HF}_2^- \leftrightarrow \text{UF}_8^{2-} + \text{HF} \]  
(7)

It is considered that the red solid formed at the beginning of the reaction is a metastable
complex salt of AgF and UF₆ which decomposes to AgF₂ and AgUF₆. While the hepta-
and octafluorouranates (VI), MUF₇ and M₂UF₈ (M = Na, K, Rb, Cs, NO, NH₄), have
been identified by X-ray diffraction[14,15], no structural informations are available for
AgUF₇ or Ag₂UF₈. If AgUF₇ is this intermediate phase, the decomposition would
proceed as follows.

\[ 2\text{AgUF}_7 \rightarrow \text{AgF}_2 + \text{AgUF}_6 + \text{UF}_6 \]  
(8)
In case that \( \text{Ag}_2\text{UF}_8 \) is the intermediate phase, the decomposition reaction would occur without the evolution of \( \text{UF}_6 \).

\[
\text{Ag}_2\text{UF}_8 \rightarrow \text{AgF}_2 + \text{AgUF}_6
\]  

(9)

Actually no evolution of \( \text{UF}_6 \) was observed from the reaction product sealed in a Pyrex glass ample. It is concluded that the red precipitate is \( \text{Ag}_2\text{UF}_8 \) which is insoluble in \( \text{HF} \) and decomposes to \( \text{AgF}_2 \) and \( \text{AgUF}_6 \). The oxidation of cationic Ag(I) to Ag(II) is considered to be accomplished through the nucleophilic attack of the fluorouranate (VI) anion. Isolation of \( \text{AgUF}_7 \) attempted by evacuating the HF quickly just before \( \text{Ag}_2\text{UF}_8 \) precipitates failed.

In Fig. 4-1 the formula volumes of several fluorouranates of monovalent metals are plotted against the cationic radii\(^{[14, 15, 16]} \). In the region where cationic radius exceeds

![Graph showing the formula volume of some \( M_x\text{UF}_y \) complex salts and ionic radius of \( M^+ \).](image-url)

Fig. 4-1 Relations between the formula volume of some \( M_x\text{UF}_y \) complex salts and ionic radius of \( M^+ \).
1.2 Å, linear relationships exist between these parameters for these penta- and hexavalent fluorouranates including Ag₂UF₆. Formula volumes of all the sodium fluorouranates deviate from this tendency taking similar sizes regardless of the types of complex salts. This is probably due to the large differences in sizes between the sodium ion and fluorouranate anions which prevent the effective close packing of the cations and anions.

The instability of Ag₂UF₆ prevented from obtaining a good X-ray powder pattern enough to refine the structure. So, here, the discussion will be limited to preliminary model structures constructed as follows. First of all, the lattice volume approximately corresponds to four times that of the formula unit. Miller indices of X-ray diffraction lines identified as those of Ag₂UF₆ are all even or odd reflections except 110 line. Therefore, the heavy atoms, silver and uranium, are presumably located on, or, at least closely to the special positions which satisfy a face-centered symmetry. Assuming UF₈²⁻ anion is spherical, it must be closely packed in the cubic lattice. From these requirements, it is automatically derived that the uranium positions must be (0, 0, 0) and (1/2, 1/2, 0) in a cubic lattice. Another heavy atom, silver should be placed at the interstitial sites of UF₈²⁻ anions such as (1/4, 1/4, 1/4) to fulfill the stoichiometry and face-centered symmetry. There is a possibility that it is slightly shifted from the special position without

(a) Cubic

(b) Square antiprism

Fig. 4-2 Geometries of octa-coordinated UF₈²⁻ anion.
significantly changing the peak intensities in the powder pattern. From these facts, the crystal structure of Ag$_2$UF$_8$ is reasonably concluded to be closely related to an inverse fluorite type. From the requirement of cubic symmetry of the lattice, at least UF$_8^{2-}$ at (0, 0, 0) should possess a cubic geometry although it is slightly less stable than the square antiprism ($D_{4d}$)[17] (Fig. 4-2). The cubic geometry has been found in M$_3$U$^{VI}$F$_8$ complex salts[18] while it has been only proposed in Na$_2$U$^{V}$F$_8$ from the results of vibrational spectroscopy[14]. Consequently, it was revealed that the possible space groups are limited to Pm$\bar{3}$m, P432 and Pm$\bar{3}$.

The optimized positional parameters of the Ag$_2$UF$_8$ structure for each space group are listed in Table 4-2. Here the geometry of UF$_8^{2-}$ is assumed to be cubic or square

<table>
<thead>
<tr>
<th>Table 4-2</th>
<th>Space groups and positional parameters of the models of Ag$_2$UF$_8$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pm$\bar{3}$m</td>
<td>Atom ( x ) ( y ) ( z )</td>
</tr>
<tr>
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<td>Ag(8g) 0.3712 0.3712 0.3712</td>
</tr>
<tr>
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<td>F1(8g) 0.1424 0.1424 0.1424</td>
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<tr>
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<td>U1(1a) 0.0000 0.0000 0.0000</td>
</tr>
<tr>
<td>U2(3c) 0.5000 0.5000 0.0000</td>
<td>U2(3c) 0.5000 0.5000 0.0000</td>
</tr>
</tbody>
</table>

Interatomic distances / Å

| Ag - F1 2.330 | Ag - F2 2.167 | Ag - F3 2.073 |
| F1 - F1 2.425 | F1 - F2 2.900 | F1 - F3 2.073 |
| F1 - U1 2.100 | F1 - F1 2.425 | F1 - F1 2.425 |
| F2 - F2 1.879 | F1 - F2 2.695 | F1 - F2 2.568 |
| F2 - F2 2.425 | F1 - U1 2.100 | F1 - U1 2.100 |
| F2 - U2 2.101 | F2 - F2 2.420 | F2 - F2 2.425 |
| F2 - F2 2.626 | F2 - F2 2.627 | F2 - F2 2.425 |
| F2 - F2 2.100 | F2 - U2 2.100 | F3 - F3 2.425 |
| F3 - U2 2.100 | F3 - F3 2.425 | F3 - U2 2.100 |

Lattice parameter: \( a_0 = 8.513 \) Å.
antiprismatic and U-F bond length to be 2.1 Å which is slightly longer than that in UF₆ (1.994 Å[16]). The schematic illustrations of these models are shown in Fig. 4-3 (a)-(c). All the geometries of UF₈²⁻ anions must be cubic in both Pm3m and Pm3 from requirement of the symmetry. In P432 lattice, UF₈²⁻ at the face center is allowed to take square antiprism geometry. In this geometry, two squares of the fluorine atoms in UF₈²⁻ are staggered to each other taking closer approach due to the decrease of repulsion. The position of silver atom was determined to maximize the distance between silver and fluorine atoms.

From the calculation of the interatomic distances in each model, the possibility of the Pm3m model is ruled out by the too small distance between the fluorine atoms (241) from adjacent two UF₈²⁻ anions at the face-centered positions (F2-F2, 1.879 Å). These fluorine atoms are apart enough in P432 and Pm3 models. In the Pm3 model, Ag-F distances are optimized to be 2.073 and 2.495 Å, the former being smaller than the sum of the ionic radii of silver and fluoride ions. On the other hand, silver and fluorine atoms are well separated in the P432 model. However, the structure is not acceptable because eight silver atoms (8g) are too closely gathered in the center of the cell. Therefore the Pm3 model is concluded to be the best candidate for a structure of Ag₂UF₈.

If the Pm3 model structure is correct, there should be appreciable covalent character between silver and fluorine atoms which explains the shorter bond length. The bond length, 2.073 Å, estimated in this model is close to that typical for covalent compounds (e.g. 2.07 Å for AgF₂[4]). The oxidation of Ag(I) to Ag(II) might occur through ligand-bridged (inner sphere) mechanism in which “active complex,” (Ag-F⁻)₂UF₆, rearranges to AgF₂ and AgUF₆.

Figure 4-4 shows a preliminary simulation of X-ray powder profile for the Pm3 model. The observed lines are marked with open circles on them. The simulation was made by RIETAN program[19] assuming the isotropic thermal parameters of 1.0 for uranium and silver atoms and 2.0 for fluorine atoms. The intensity of (100) line was not
Fig. 4-3 Examined crystal structure models of Ag$_2$UF$_6$. 
Fig. 4-4  Simulated X-ray powder profile of Ag$_2$UF$_8$ assuming the Pm$\bar{3}$ model. The
peaks with open circles are observed by X-ray diffraction. Peaks with X
should overlay with those of AgUF$_6$ and AgF$_2$.

collected in the pattern due to the geometrical limitation of the powder camera. The
matching of the relative peak intensities in the observed and simulated patterns are not
good enough. A further examination to obtain a better powder pattern profile is necessary
for determination of the detailed structure of Ag$_2$UF$_8$.

The direct fluorination of xenon by UF$_6$ is thermodynamically unfavorable. The
fluorination reaction of xenon by UF$_6$ in AgF solution of HF was examined since the free
enthalpy change of the following reaction is calculated to be $-16 \pm 20$ kJ mol$^{-1}$.

$$2\text{AgF} + 2\text{UF}_6 + \text{Xe} \rightarrow \text{XeF}_2 + 2\text{AgUF}_6$$ (10)

The formation of XeF$_2$ was however, not actually observed at ambient temperature. It is
not clear that the failure of this reaction is due to whether a thermodynamic or kinetic
reason. From this result, the possibility of the formation of Ag(II)-U(VI) complex salt
like $\text{AgFUF}_7$ or $\text{AgUF}_8$ from $\text{AgF}_2$ and $\text{UF}_6$ is also denied since the cationic $\text{Ag(II)}$ oxidizes xenon to $\text{Xe(II)}$ in HF\cite{3,7,8}:

$$\text{AgF}_2 + \text{UF}_6 \rightarrow \text{AgFUF}_7 \text{ or } \text{AgUF}_8 \quad (11)$$

The fluoride ion affinity of $\text{UF}_6$ would be too low to stabilize the $\text{AgF}^+$ or $\text{Ag}^{2+}$ ion. Although the fluoride ion affinity of the $\text{UF}_5$ is much higher than $\text{UF}_6$, $\text{U(V)}$ is easily oxidized to $\text{U(VI)}$ by cationic $\text{Ag(II)}$ in HF.

$$\text{AgFBF}_4 + \text{UF}_5 \rightarrow \text{AgBF}_4 + \text{UF}_6 \quad (12)$$

So it is obvious that the formation of the $\text{Ag(II)-U(V)}$ complex salt such as $\text{AgFUF}_6$ or $\text{AgUF}_7$ does not occur.
References


16. D. Brown, "Halides of the Lanthanides and Actinides," Chapt. 2, Fluorides and...
Oxyfluorides, John Wiley & Sons Ltd., (1968) and references contained therein.


CHAPTER 5
Reactions of uranyl fluoride with some fluorobases
in anhydrous hydrogen fluoride*

5.1 Introduction

Uranyl fluoride ($\text{UO}_2\text{F}_2$) is an ionic compound containing a uranyl cation ($\text{UO}_2^{2+}$), surrounded by 6 fluoride ions with a distance of 2.50 Å. Some complex ions, $\text{UO}_2\text{F}_{2n}^{n-}$ ($n = 1, 2, 3$), have been found by spectroscopic measurements in aqueous solutions of $\text{UO}_2\text{F}_2$ containing a fluorobase such as KF[1]. In fact, the concentration of fluoride ion in the aqueous solution of $\text{UO}_2\text{F}_2$ is unable to be measured precisely by a fluoride ion selective electrode because of the complex formation.

Anhydrous $\text{MUO}_2\text{F}_3$ and $\text{M}_2\text{UO}_2\text{F}_5$ ($\text{M}$: singly charged metals) are obtained from their hydrates prepared in aqueous solution[2]. The structure of $\text{UO}_2\text{F}_5^{3-}$ ion in $\text{M}_2\text{UO}_2\text{F}_5$ ($\text{M} = \text{K}, \text{NH}_4$ and Cs) has been reported. On the other hand, $\text{UO}_2\text{F}_5^{-}$ ion in $\text{MUO}_2\text{F}_3$ ($\text{M} = \text{Cs}$) has not been characterized. Double salts, $\text{K}_3(\text{UO}_2)_2\text{F}_7$ and $\text{K}_5(\text{UO}_2)_2\text{F}_9$, also have been prepared in aqueous solution[2]. The reaction of $\text{UO}_2\text{F}_2$ and silver(I) fluoride ($\text{AgF}$) in acetone has been found to form $\text{Ag(UO}_2)_2\text{F}_5[3]$. In this chapter, fluoroacidity of $\text{UO}_2\text{F}_2$ is discussed based on the results on the reactions with alkaline metal fluorides and AgF in anhydrous hydrogen fluoride (HF). The compounds obtained were characterized by X-ray powder diffraction and vibrational spectroscopy.

5.2 Reagents

AgF was prepared in the same manner as described in Chapter 3. CsF (Nakarai Tesque, extra pure reagent) and KF (Wako Chemicals, purity 98% or more) were dried under vacuum at ~300°C. U₃O₈ was obtained by heating UO₂ (Furukawa Denki Kogyo, depleted uranium) in an alumina crucible in air at ~800°C. UO₂F₂ was prepared by fluorinating U₃O₈ in a Monel container at 200°C.

5.3 Results

CsF + UO₂F₂

CsF (176 mg, 1.16 mmol) and UO₂F₂ (355 mg, 1.15 mmol) were interacted in HF (~1 cm³) at room temperature. On stirring for several hours, a pale yellow solid was obtained after evacuating volatile materials at room temperature. A small weight uptake (26 mg, 1.3 mmol as HF) was observed. The X-ray powder pattern of the solid obtained after successive evacuation at ~70°C was identical with that of CsUO₂F₃ prepared in aqueous solution[4]. The Raman spectrum of CsUO₂F₃ could not be obtained due to the strong fluorescence of the sample.

KF + UO₂F₂

KF (32 mg, 0.55 mmol) and UO₂F₂ (172 mg, 0.56 mmol) were interacted in HF (~1 cm³) at room temperature. After stirring for several hours, a light green solid was obtained after evaporating HF very slowly. X-ray diffraction showed that the solid was a mixture of K₃UO₂F₅[5] and UO₂F₂. The Raman spectrum of K₃UO₂F₅ could not be obtained due to the strong fluorescence of the sample.
\( \text{AgF} + \text{UO}_2\text{F}_2 \)

AgF (35 mg, 0.28 mmol) and \( \text{UO}_2\text{F}_2 \) (85 mg, 0.28 mmol) were interacted in HF at room temperature. A light yellow solid was obtained after stirring for 20 hours. No weight uptake was observed after removing volatile materials. X-ray diffraction showed no peaks corresponding to the starting materials. The solid is considered to be the 1 : 1 compound of AgF and \( \text{UO}_2\text{F}_2 \) by the vibrational spectra of the solid.

\( 3\text{AgF} + \text{UO}_2\text{F}_2 \)

AgF (233 mg, 1.84 mmol) and \( \text{UO}_2\text{F}_2 \) (189 mg, 0.614 mmol) were loaded in one arm (Tube A) of a T-shaped reactor and interacted in HF (\( \sim 2 \text{ cm}^3 \)) at room temperature. After stirring for several hours, the supernatant solution over the precipitate was decanted to Tube B and the precipitate was washed several times with HF which was condensed back to Tube A. A light yellow solid in Tube A was obtained by removing volatile materials and a colorless solid in Tube B was crystallized from the solution used for washing the precipitate. The color of the solid turned to bright yellow by the additional evacuation while warming Tube B. X-ray diffraction showed that the solid in Tube A was the mixture of \( \text{UO}_2\text{F}_2 \) and the 1 : 1 compound obtained by the interaction of AgF + \( \text{UO}_2\text{F}_2 \). The solid in Tube B was only AgF.

\textit{Excess AgF + UO}_2\textit{F}_2

\( \text{UO}_2\text{F}_2 \) (145 mg, 0.471 mmol) was placed in one arm (Tube A) of a T-shaped reactor and AgF (654 mg, 5.15 mmol) in the other arm (Tube B). HF (\( \sim 1 \text{ cm}^3 \)) was condensed in Tube B to prepare a saturated solution of AgF with a trace amount of white precipitate. The solution was decanted to Tube A and the mixture was stirred for several hours. The supernatant solution was decanted to Tube B. In Tube A, a bright yellow solid was obtained after evacuating HF with heating so as to decompose \( \text{Ag(HF)}_n\text{F} \). X-ray diffraction showed that the solid in Tube A was a mixture of AgF and the 1 : 1 compound
of AgF and UO$_2$F$_2$ and that the solid remained in Tube B was only AgF.

5.4 Discussion

UO$_2$F$_2$ acts as a fluoroacid to give some compounds with MF (M : univalent metal) in aqueous solutions[2]. The anhydrous 1 : 1 compound prepared so far is only CsUO$_2$F$_3$[4] the structure of which has not yet been determined. The existence of the complex anion, UO$_2$F$_7^-$, has not been claimed in the solid state although it was identified in the gaseous phase by Knudsen's effusion method in combination with mass-spectrometry[6] and in the solution by Raman spectroscopy[1]. The formation of some oxofluorocomplex anions is expected in M$_3$UO$_2$F$_5$ and MUO$_2$F$_3$ since the uranium atom in UO$_{2}^{2+}$ is coordinated by ligands forming strong bonds with some covalency[7]. In fact, the anhydrous 3 : 1 compounds, M$_3$UO$_2$F$_5$ (M = K, Cs and NH$_4$), are well characterized and a pentagonal bipyramidal anion, UO$_2$F$_5^{2-}$, was found in K$_3$UO$_2$F$_5$[5]. In this anion, five fluorine atoms coordinate to uranium atom within the plane perpendicular to the linear O-U-O axis to form a regular pentagon (Fig 5-1).

In the reaction of equimolar amounts of CsF and UO$_2$F$_2$ in HF, the solvated salt, CsUO$_2$F$_3$·nHF, seems to be formed like the hydrate prepared from the aqueous solution.

![Dioxopentfluorouranate anion in K$_3$UO$_2$F$_5$.](image_url)

Fig. 5-1  Dioxopentfluorouranate anion in K$_3$UO$_2$F$_5$. 

50
This compound loses HF at \( \sim 70^\circ C \) to give CsUO\(_2\)F\(_3\). On the other hand, the reaction of equimolar amounts of KF and UO\(_2\)F\(_2\) in HF does not give the 1 : 1 compound, KUO\(_2\)F\(_3\), but the mixture of K\(_3\)UO\(_2\)F\(_5\) and unreacted UO\(_2\)F\(_2\).

A novel 1 : 1 compound, AgUO\(_2\)F\(_3\), is formed by the reaction of equimolar amounts of AgF and UO\(_2\)F\(_2\) in HF. The X-ray powder pattern of AgUO\(_2\)F\(_3\) is shown in Table 5-1. It is suggested that AgUO\(_2\)F\(_3\) contains some oxofluoroanions from the vibrational spectra as shown in Fig. 5-2 and Table 5-2. If the uranium were present only in the form of bare cationic UO\(_2^{2+}\), a single peak around 900 cm\(^{-1}\) should be observed in the Raman spectrum. The possibility of formation of a double salt containing UO\(_2^{2+}\) is excluded from the spectrum of the sample.

AgUO\(_2\)F\(_3\) is solvolyzed by washing with HF:

\[
\text{AgUO}_2\text{F}_3 + n\text{HF} \rightleftharpoons \text{Ag}^+ + (\text{HF})_n\text{F}^- + \text{UO}_2\text{F}_2
\]

In order to obtain a pure sample of AgUO\(_2\)F\(_3\), it is necessary to remove HF very slowly from the system to shift the equilibrium to the left. The growth of a single crystal is

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<tr>
<th>(d / \text{Å} )</th>
<th>Intensity</th>
<th>(d / \text{Å} )</th>
<th>Intensity</th>
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<td>2.52 w</td>
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</tbody>
</table>

Abbreviations used: s, strong; m, medium; v, very; w, weak.
practically impossible in HF due to the low solubility of AgUO$_2$F$_3$.

The reaction of CsF with UO$_2$F$_2$ gives both the 3:1 and 1:1 compounds in aqueous solution, however, only the latter being formed in HF. Only the 3:1 compound is formed by the reaction of KF and UO$_2$F$_2$ in both the solutions. The reaction of AgF and UO$_2$F$_2$ in HF provides only the 1:1 compound even in HF saturated with AgF. These observations cannot be explained by the simple comparative chemistry of the stability of ionic salts.

The fluoroacidity of UO$_2$F$_2$ in HF does not seem to be exceedingly higher than that
of HF due to the low solubility as expected from its fluoride ion affinity slightly higher than that of HF\[6,8\]. The stabilities of the compounds of \( \text{UO}_2\text{F}_2 \) with strong fluorobases such as \( \text{MF} \) (\( M = \text{K}, \text{Cs} \text{ and } \text{Ag} \)) are higher than those of \( \text{M(HF)}_n\text{F} \). However, the solvolysis of the compounds seems to occur in excess HF resulting in precipitating \( \text{UO}_2\text{F}_2 \) as observed in the reaction of \( \text{AgF} \) and \( \text{UO}_2\text{F}_2 \).

Table 5-2 Vibrational spectra of \( \text{AgUO}_2\text{F}_3 \). Frequencies are given in cm\(^{-1}\). Abbreviations used: sh, sharp; br, broad; s, strong; m, medium; v, very; w, weak.

<table>
<thead>
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CHAPTER 6

Reactions of uranyl fluoride with some fluoroacids in anhydrous hydrogen fluoride

6.1 Introduction

Property of uranyl fluoride (UO$_2$F$_2$) as a fluoroacid in anhydrous hydrogen fluoride (HF) has been discussed in Chapter 5. UO$_2$F$_2$ is an ionic compound containing uranyl cation, UO$_2^{2+}$. The lattice energy of UO$_2$F$_2$, 2315 kJ mol$^{-1}$[1], is a little smaller than that of barium fluoride (BaF$_2$, 2352 kJ mol$^{-1}$[2]). Thus, UO$_2$F$_2$ is expected to act as a fluorobase like BaF$_2$ in HF. However, it has been examined only for the reactions with HF-SbF$_5$ system[3,4] which is one of the strongest superacids.

Preparation of a mixed valence compound, U$_2$O$_4$F$_7$, is expected to be made by the acid-base reaction of UO$_2$F$_2$ and UF$_5$ in HF. U$_2$O$_2$F$_7$ has been prepared by the reaction of U$^{IV}$O$_2$F$_2$ with U$^{V}$F$_5$ under ~3 atm of UF$_6$ atmosphere at 370°C[5]. However, it has not been characterized enough. UF$_5$ acts as a fluoroacid in HF by forming UF$_6^-$ anion, the fluoride ion affinity (~423 kJ mol$^{-1}$[6,7]) of which being comparable to that of PF$_5$. It also acts as a dibasic and tribasic fluoroacid by forming UF$_7^{2-}$ and UF$_8^{3-}$ anions, respectively. The complex salts of UF$_5$ and some fluorobases have been prepared in HF[8]. On the other hand, UF$_5$ acts as a fluorobase when it is interacted with strong fluoroacids, such as SbF$_5$ and AsF$_5$, forming some adducts, UF$_5$nSbF$_4$ and UF$_5$nAsF$_5$[9]. It is important to examine the property of UO$_2$F$_2$ as a fluorobase in order to clarify the reaction of UO$_2$F$_2$ and UF$_5$.

In this chapter, the properties of UO$_2$F$_2$ as a fluorobase in HF are studied by the reactions with some fluoroacids, BF$_3$, PF$_5$, TaF$_5$, GeF$_4$, AsF$_5$, BiF$_5$ and UF$_5$. The

* A part of this chapter was published in *J. Fluorine Chem.*, Vol. 74, No. 1, 89 (1995).
discussion will be made on the compounds obtained by these reactions.

6.2 Reagents

F₂ (Daikin Kogyo, purity 99.7%), PF₅ (Nippon Sanso), TaF₅ (Ozark-Mahoning), AsF₅ (Matheson) and BF₃ (Nippon Sanso) were used as supplied. GeF₄ was prepared by fluorinating powdered Ge metal in a Monel container at 300°C, and distilled into another container after evacuating volatile gases at -196°C for a while. Antimony pentafluoride (SbF₅, PCR, purity 97%) was used for reactions by distillation to avoid the contamination of SbF₃. BiF₄ was prepared by fluorination of Bi₂O₃ (Nakarai Tesque, purity 99.9%) and purified by vacuum sublimation at ~70°C. Commercially supplied BiF₅ (Ozark-Mahoning, purity 97%) was also used without further purification. UO₂F₂ was prepared in the same manner as described in Chapter 5. Preparation of β-UOF₃ is described in Chapter 4.

6.3 Results

\( UO₂F₂ + \text{excess AsF₅} \)

UO₂F₂ (190 mg, 0.617 mmol) was interacted with excess AsF₅ in HF (~2 cm³) at room temperature. UO₂F₂ dissolves immediately to give a yellow solution. On evacuating HF slowly, a yellow-green solid was precipitated. Although a significant weight uptake (81 mg, 0.48 mmol as AsF₅) was observed just after the reaction, X-ray diffraction on the final product showed only the pattern of UO₂F₂.

\( UO₂F₂ + \text{liquid AsF₅ without HF solvent} \)

UO₂F₂ (244 mg, 0.792 mmol) was placed in a reaction tube and AsF₅ (~1 cm³) was condensed on it at -77°C. UO₂F₂ was not dissolved in this case. After stirring the mixture
for 2 hours, a green solid was formed. The color of the remaining solid after evacuating excess AsF₅ at −77°C faded and the pressure in the tube increased with elevation of the temperature. The amount of the released gas was estimated to be about 1.3 mmol by tensimetry. IR spectroscopy showed that the gas was pure AsF₅. X-ray diffraction revealed that the residual solid was UO₂F₂.

\[ UO₂F₂ + \text{excess } BF₃ \]

UO₂F₂ (447 mg, 1.45 mmol) was interacted with excess BF₃ in HF (~2 cm³) at room temperature. The color change of the precipitate, gas consumption and weight uptake were not observed. X-ray diffraction identified only UO₂F₂ in the solid.

\[ UO₂F₂ + \text{excess } GeF₄ \]

UO₂F₂ (423 mg, 1.37 mmol) was interacted with excess GeF₄ in HF (~2 cm³) at room temperature. A green precipitate was formed after stirring the liquid for a while. The color of the solid faded on evacuating HF. No weight change was observed after the reaction. X-ray diffraction showed that the residual solid was UO₂F₂.

\[ UO₂F₂ + \text{TaF₅} \]

UO₂F₂ (389 mg, 1.26 mmol) was interacted with TaF₅ (704 mg, 2.55 mmol) at room temperature for ~20 hours in HF. Dissolution of UO₂F₂ was not observed during the reaction. X-ray diffraction identified UO₂F₂ and TaF₅ in the solid remained after evacuation of HF.

\[ UO₂F₂ + 2BiF₃ \]

UO₂F₂ (110 mg, 0.357 mmol) was interacted with BiF₃ (209 mg, 0.688 mmol) at room temperature for ~20 hours in HF. A yellow green precipitate was formed and the supernatant solution slightly colored yellow. An yellow green solid was obtained after
evacuating HF. No weight change was observed after the reaction. X-ray powder diffraction detected no starting materials.

\[ \text{UO}_2\text{F}_2 + \text{BiF}_5 \]

\( \text{UO}_2\text{F}_2 (160 \text{ mg, 0.519 mmol}) \) and \( \text{BiF}_5 (158 \text{ mg, 0.520 mmol}) \) were reacted in HF for ~20 hours at room temperature. An yellow green solid was obtained after evacuating HF. No weight change was observed after the reaction. X-ray powder diffraction pattern showed that the solid was the mixture of \( \text{UO}_2\text{F}_2 \) and the compound prepared by the reaction of \( \text{UO}_2\text{F}_2 + 2\text{BiF}_5 \).

\[ \text{UO}_2\text{F}_2 + 3\text{BiF}_5 \]

\( \text{UO}_2\text{F}_2 (40 \text{ mg, 0.13 mmol}) \) and \( \text{BiF}_5 (111 \text{ mg, 0.365 mmol}) \) were reacted in HF for ~20 hours at room temperature. An yellow green solid was obtained after evacuating HF. No weight change was observed after the reaction. X-ray powder diffraction showed that the solid was the mixture of \( \text{BiF}_5 \) and the compound prepared in the reaction of \( \text{UO}_2\text{F}_2 + 2\text{BiF}_5 \).

\[ \text{UO}_2\text{F}_2 + \text{UF}_5 \]

\( \text{UO}_2\text{F}_2 (54 \text{ mg, 0.18 mmol}) \) and \( \beta\text{-UF}_5 (54 \text{ mg, 0.17 mmol}) \) were reacted in HF for ~48 hours at room temperature. No weight change was observed after the reaction. X-ray powder diffraction detected only \( \text{UO}_2\text{F}_2 \) and \( \text{UF}_5 \).

\[ \text{UO}_2\text{F}_2 + \text{excess SbF}_5 \]

\( \text{UO}_2\text{F}_2\cdot2\text{SbF}_5 \) was prepared by the following procedures as described in ref. 3: \( \text{UO}_2\text{F}_2 (652 \text{ mg, 2.12 mmol}) \) was interacted with excess \( \text{SbF}_5 \) in HF for ~20 hours at room temperature. \( \text{UO}_2\text{F}_2 \) was readily dissolved completely to give a yellow solution. After evacuating HF and \( \text{SbF}_5 \), a yellow green solid was obtained. The solid was
determined to be UO$_2$F$_2$.3SbF$_5$ by the weight uptake of the sample (1411 mg, 6.511 mmol as SbF$_5$). Then, UO$_2$F$_2$.3SbF$_5$ (393 mg, 0.410 mmol) was decomposed under dynamic vacuum at -140°C, giving a yellow green solid. From the weight, the composition was estimated to be UO$_2$F$_2$.1.6SbF$_5$. A small amount of UO$_2$F$_2$ was contaminated in the sample by further decomposition of UO$_2$F$_2$.2SbF$_5$.

6.4 Discussion

Although UO$_2$F$_2$ is insoluble in liquid HF, it dissolves when HF is acidified by AsF$_5$, the solution giving the typical yellow color of UO$_2^{2+}$. However, the compound of UO$_2$F$_2$ and AsF$_5$ formed at -77°C in HF is not stable at room temperature and decomposes to UO$_2$F$_2$ and AsF$_5$. Based on the amount of the released AsF$_5$, the UO$_2$F$_2$ / AsF$_5$ ratio of the compound is approximately 1 : 2. It is known that the reaction of UO$_2$F$_2$ and SbF$_5$ in HF gives several compounds stable at room temperature, UO$_2$F$_2$.nSbF$_5$ (n = 2, 3, 4)[3,4].

UO$_2$F$_2$.3SbF$_5$ is characterized as an ionic solid containing monomeric SbF$_6^{-}$ and dimeric Sb$_2$F$_{11}^{-}$, UO$_2^{2+}$SbF$_6^{-})$Sb$_2$F$_{11}^{-}$[3]. UO$_2$F$_2$.2SbF$_5$ is presumably expressed as UO$_2^{2+}$SbF$_6^{-})_2$ from the comparison of its IR spectrum with that of UO$_2$F$_2$.3SbF$_5$. The enthalpy change of the decomposition of UO$_2$F$_2$.2AsF$_5$ is estimated from that of UO$_2$F$_2$.2SbF$_5$ at 245°C[3] taking account of the difference in the fluoride ion affinities of SbF$_5$ and AsF$_5$[10,11]. The estimation here is made assuming; a) the lattice energies of UO$_2$F$_2$.2SbF$_5$ and UO$_2$F$_2$.2AsF$_5$ are approximately the same because of the similarity of the molecular volumes of SbF$_6^{-}$ and AsF$_6^{-}$, b) the difference in enthalpy changes of the decomposition of UO$_2$F$_2$.2SbF$_5$ at room temperature and 245°C is negligible.

The entropies of UO$_2$F$_2$(s), SbF$_5$(g) and AsF$_5$(g) are literally available[12] and those of UO$_2$F$_2$.2SbF$_5$(s) and UO$_2$F$_2$.2AsF$_5$(s) were evaluated by Latimer's method[13]. The free enthalpy changes of the reactions of UO$_2$F$_2$ with SbF$_5$ and AsF$_5$ at room
temperature are evaluated by combining the enthalpy changes and entropies estimated above:

\[
\begin{align*}
\text{(1)} & \quad \Delta G^\circ = -169 \text{ kJ mol}^{-1} \\
\text{(2)} & \quad \Delta G^\circ = 9 \text{ kJ mol}^{-1}
\end{align*}
\]

The \(\Delta G^\circ\) values agree with the observations that \(\text{UO}_2\text{F}_2\cdot2\text{SbF}_5\) is stable while \(\text{UO}_2\text{F}_2\cdot2\text{AsF}_5\) is not which decomposes to \(\text{UO}_2\text{F}_2\) and \(\text{AsF}_5\) at room temperature. The difference in the stabilities is mainly due to the difference in the fluoride ion affinities. The reaction of \(\text{UO}_2\text{F}_2\) and \(\text{TaF}_5\) does not give a compound, the fluoride ion affinity of the latter being smaller than that of \(\text{AsF}_5\).

\(\text{UO}_2\text{F}_2\) does not react with \(\text{BF}_3\) to give a stable compound. The lattice energy of the complex salt of \(\text{UO}_2\text{F}_2\) and \(\text{BF}_3\) is expected to be larger than those of \(\text{SbF}_5^-\) and \(\text{AsF}_6^-\) salts because of the smaller volume of \(\text{BF}_3^-\). However, the fluoride ion affinity of \(\text{BF}_3\) is weak compared to \(\text{AsF}_5\) and \(\text{SbF}_5\), which offsets this advantage for the formation of the complex salt.

The reaction of \(\text{UO}_2\text{F}_2\) with \(\text{GeF}_4\) appears to proceed in \(\text{HF}\), however, the salt is not stable. The fluoroacidity of \(\text{GeF}_4\) by accepting two fluoride ions to form \(\text{GeF}_6^{2-}\) is probably not strong enough to form a complex salt, \(\text{UO}_2^{2+}\text{GeF}_6^{2-}\), in spite of the advantage of the larger lattice energy which arises from the doubly charged ions. Even if \(\text{GeF}_4\) acts as a monobasic fluoroacid, its fluoroacidity is weaker than that of \(\text{AsF}_5\), the complex salt such as \(\text{UO}_2^{2+}(\text{GeF}_5^-)_2\) not being stabilized.

The reaction of \(\text{UO}_2\text{F}_2\) with \(\text{BiF}_5\) gives only a 1:2 compound, \(\text{UO}_2\text{F}_2\cdot2\text{BiF}_5\), while several compounds, \(\text{UO}_2\text{F}_2\cdot\text{nSbF}_5\) (\(n = 2, 3, 4\)), are known as mentioned above. The stable complex salts containing a dimeric anions of \(\text{BiF}_5\), \(\text{Bi}_2\text{F}_{11}^-\), have not been reported. The X-ray powder patterns of \(\text{UO}_2\text{F}_2\cdot2\text{BiF}_5\) and \(\text{UO}_2\text{F}_2\cdot2\text{SbF}_5\) are shown in Table 6-1. As can be seen from the table, \(\text{UO}_2\text{F}_2\cdot2\text{BiF}_5\) is isomorphous with \(\text{UO}_2\text{F}_2\cdot2\text{SbF}_5\). IR spectrum of \(\text{UO}_2\text{F}_2\cdot2\text{BiF}_5\) is shown in Fig. 6-1. The similarity in the spectra of \(\text{UO}_2\text{F}_2\cdot2\text{BiF}_5\) and \(\text{UO}_2\text{F}_2\cdot2\text{SbF}_5\) (Fig 6-1) also supports that geometrically closely related molecular entities.
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*Impurity ascribed to $\text{UO}_2\text{F}_2$ formed by subsequent decomposition of $\text{UO}_2\text{F}_2\cdot\text{SbF}_5$. 

Table 6-1 X-ray powder patterns of $\text{UO}_2\text{F}_2\cdot\text{BiF}_3$ and $\text{UO}_2\text{F}_2\cdot\text{SbF}_5$. 

61
exist in both the compounds. The peak corresponding to the asymmetric stretching of O-U-O (1004 cm\(^{-1}\)) in UO\(_2\)F\(_2\).2SbF\(_5\) is shifted to a lower wavenumber (990 cm\(^{-1}\)) in UO\(_2\)F\(_2\).2BiF\(_5\). This suggests that uranium is less positively charged in UO\(_2\)F\(_2\).2BiF\(_5\), therefore the fluoride ion affinity of BiF\(_5\) is lower than that of SbF\(_5\). On the other hand, the instability of UO\(_2\)F\(_2\).2AsF\(_5\) compared to UO\(_2\)F\(_2\).2BiF\(_5\) suggests that the fluoride ion affinity of BiF\(_5\) is larger than that of AsF\(_5\).
UO₂F₂ is concluded to be a weak fluorobase in HF reacting only with strong fluoroacids such as AsF₅, BiF₃ and SbF₅. The reaction of UO₂F₂ with UF₅ does not give a compounds like UO₂F₂·2UF₅ since the fluoride ion affinity of UF₅ is smaller than that of AsF₅[6,7] and not enough to withdraw the second fluoride ion from UO₂F₂. However, several compounds, such as MF₂·2UF₅ (M = Ba, Sr, Zn, Sn and Co, probably M(UF₆)₂), have been reported to be formed by the reactions of MF₂ and UF₅ in HF[14] although the lattice enthalpies of MF₂ are not less than that of UO₂F₂. Formation of MF₂·2UF₅ would be assisted by the fluorobasicity of MF₂ in HF and the stability of the compound. The fluorobasicity of UO₂F₂ insoluble in HF is not so strong as is expected from the lattice enthalpy. This would be the reason why formation of U₂O₂F₇ like (UO₂F)⁺UF₅⁻ or UO₂²⁺UF₇²⁻ does not occur by the reaction of UO₂F₂ and UF₅ in HF at room temperature.
References


CHAPTER 7

Acid-base reactions of rare earth trifluorides
in anhydrous hydrogen fluoride

7.1 Introduction

Rare earth (RE) elements exhibit similar chemical behaviors because of their similarities in sizes and stable trivalent oxidation states. This makes the mutual separation of RE elements difficult. Rare earth trifluorides (REF₃) are stable ionic compounds and not soluble in water or anhydrous hydrogen fluoride (HF). However, they dissolve in highly acidic solutions, such as HF-BF₃ and HF-AsF₅. Moreover, it has been reported that the divalent oxidation states, unstable in aqueous solutions, is stabilized in anhydrous HF[1].

Several compounds of REF₃ and alkaline metal fluorides (MF) are also prepared from their fused melts[2]. The crystal structure of MREF₄ (hexagonal, space group P6₃) shows that these compounds are not complex salts in which the fluoroanions of rare earth elements are involved but double salts of MF and REF₃ since the bond lengths of RE and fluorine atoms correspond to the sum of the individual cationic and anionic radii of them[3]. On the other hand, two types of the crystal structures of M₂REF₆ have been reported by Reshetnikova et al.[4]. One of them is a cubic, α-K₃AlF₆ type (Fm3m[5]) and the other is a tetragonal, Cs₃YF₆ type (I4/mmm[6]). In both cases, the existence of REF₆ octahedra was identified by the ν₃ mode in IR spectra. Whether the compounds M₂REF₆ are complex or double salts is still controversial since the detailed crystal structures have not been obtained.

REF₃ acts as a fluorobase in highly acidic condition as described above. Clifford et

* To be submitted to J. Fluorine Chem.
al. have reported the formation of rare earth fluoroantimonates in HF-SbF₅[7]. Recently, formation of rare earth fluoroborates and fluoroarsenates were reported by Lutar et al. although the detailed characterization is still under way because of its difficulty[8].

This chapter deals with the reactions of rare earth trifluorides with some fluorobases and fluoroacids. The reactions and compounds are discussed based on the results of gravimetry, X-ray diffraction and vibrational spectroscopy.

7.2 Reagents

REF₃'s were obtained from Wako Chemicals (purity 99.5%) and dried under vacuum at 300°C until the pressure above the samples became less than 10⁻³ torr. Some REF₃'s were prepared by the reaction of HF with their trichloride hexahydrates (Wako Chemicals, purity 99.5%). The hexahydrates were dehydrated in the same manner as will be described in Chapter 8. Sodium, potassium and cesium fluorides (NaF, KF and CsF, Nakarai Tesque, more than 98 %) were dried under vacuum at 300°C. Silver fluoride (AgF) was prepared in the same manner as described in Chapter 2. Boron trifluoride (BF₃, Nippon Sanso, purity 99.8%) and bismuth pentafluoride (BiF₅, Ozark-Mahoning, purity 97 %) were used as supplied. Antimony pentafluoride (SbF₅, PCR, purity 97 %) was distilled to eliminate SbF₃. The purity of solid materials was checked by X-ray powder diffraction. The purity of gaseous reagents was checked by IR spectroscopy. The compounds obtained were characterized by gravimetry, X-ray diffraction, ICP (Inductively Coupled Plasma) and vibrational spectroscopy.

7.3 Results

PrF₃ + MF (M = Na, K, Cs and Ag)

The mixtures of PrF₃ and MF (M = Na, K, Cs and Ag) in an FEP reactor was
interacted in HF (−2 cm³) with stirring for several hours at room temperature. The supernatant solution was not colored in each case. After removal of liquid HF by pumping, the reactor was subsequently evacuated with elevating temperature to −80°C. In the case of AgF, the silver bifluoride was decomposed by elevating temperature which caused the change of color of the solid. The phases in the solids were identified by X-ray powder diffraction. The initial conditions and results are summarized in Table 7-1.

\[ \text{REF}_3 + \text{BF}_3 \]

REF₃ was interacted with BF₃ in HF (−2 cm³) for several hours at room temperature. The dissolution of PrF₃ and NdF₃ was observed by coloring of the solutions. A solid was obtained after evacuating excess BF₃ and HF. The initial conditions and results of gravimetry and X-ray powder diffraction are summarized in Table 7-2.

Table 7-1 Initial conditions and results of the reactions of MF and PrF₃.

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<td>PrF₃, AgF</td>
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Table 7-2 Initial conditions and results of the reactions of REF₃ and BF₃.

<table>
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<tr>
<th>REF₃</th>
<th>Initial amount of REF₃ time</th>
<th>Reaction weight uptake</th>
<th>Weight of BF₃ / REF₃</th>
<th>Phases detected by X-ray diffraction</th>
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<tr>
<td></td>
<td>mg (mmol)</td>
<td>mg</td>
<td></td>
<td>REF₃, nBF₃, REF₃</td>
</tr>
<tr>
<td>YF₃</td>
<td>115 (0.788) 1 day</td>
<td>81</td>
<td>1.5</td>
<td>Obs.</td>
</tr>
<tr>
<td></td>
<td>180 (1.23) 1 day</td>
<td>104</td>
<td>1.25</td>
<td>Obs.</td>
</tr>
<tr>
<td>LaF₃</td>
<td>132 (0.673) 3 days</td>
<td>83.2</td>
<td>1.82</td>
<td>Obs.</td>
</tr>
<tr>
<td>LaF₃</td>
<td>220 (1.12) 1 day</td>
<td>194</td>
<td>2.55</td>
<td>Obs.</td>
</tr>
<tr>
<td>CeF₃</td>
<td>240 (1.22) 1 day</td>
<td>42</td>
<td>0.51</td>
<td>Obs.</td>
</tr>
<tr>
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<td>206 (1.05) 3 days</td>
<td>45</td>
<td>0.64</td>
<td>Obs.</td>
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<tr>
<td>PrF₃</td>
<td>212 (1.07) 1 day</td>
<td>139</td>
<td>1.91</td>
<td>Obs.</td>
</tr>
<tr>
<td></td>
<td>203 (1.03) 3 days</td>
<td>161</td>
<td>2.32</td>
<td>Obs.</td>
</tr>
<tr>
<td>CeF₃</td>
<td>268 (1.35) 5 days</td>
<td>190</td>
<td>2.07</td>
<td>Obs.</td>
</tr>
<tr>
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<td>155 (0.783) 1 day</td>
<td>60</td>
<td>1.1</td>
<td>Obs.</td>
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<td>NdF₃</td>
<td>254 (1.26) 2 days</td>
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<td>2.41</td>
<td>Obs.</td>
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<td>SmF₃</td>
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<td>Obs.</td>
</tr>
<tr>
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<td>197 (0.950) 1 day</td>
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<td>2.20</td>
<td>Obs.</td>
</tr>
<tr>
<td>EuF₃</td>
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<td>0.69</td>
<td>Obs.</td>
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<td>EuF₃</td>
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<td>2.26</td>
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<td>248 (1.16) 1 days</td>
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<td>1.96</td>
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</tr>
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<td>TbF₃</td>
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<td>28</td>
<td>0.376</td>
<td>Obs.</td>
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<td>TmF₃</td>
<td>121 (0.560) 1 day</td>
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<td>1.8</td>
<td>Obs.</td>
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<td>DyF₃</td>
<td>156 (0.711) 1 day</td>
<td>48</td>
<td>1.0</td>
<td>Obs.</td>
</tr>
<tr>
<td></td>
<td>238 (1.08) 4 days</td>
<td>129</td>
<td>1.76</td>
<td>Obs.</td>
</tr>
<tr>
<td>HoF₃</td>
<td>239 (1.08) 2 days</td>
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<td>ErF₃</td>
<td>176 (0.786) 1 day</td>
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<td>ErF₃</td>
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<td>0</td>
<td>0</td>
<td>Obs.</td>
</tr>
<tr>
<td>TmF₃</td>
<td>403 (1.78) 4 days</td>
<td>6</td>
<td>0.05</td>
<td>Obs.</td>
</tr>
<tr>
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<td>245 (1.07) 1 day</td>
<td>3</td>
<td>0.04</td>
<td>Obs.</td>
</tr>
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<td>LuF₃</td>
<td>191 (0.830) 5 days</td>
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<td>1.5</td>
<td>Obs.</td>
</tr>
<tr>
<td></td>
<td>255 (1.10) 1 day</td>
<td>25</td>
<td>0.34</td>
<td>Obs.</td>
</tr>
</tbody>
</table>

*a prepared from the corresponding trichloride.

b isomorphous pattern was obtained (Orthorhombic).
PrF$_3$ + BiF$_5$

PrF$_3$ (126 mg, 0.637 mmol) and BiF$_5$ (586 mg, 1.93 mmol) were interacted in HF (~2 cm$^3$) for ~20 hours at room temperature. The dissolution of PrF$_3$ was observed by the green color of the supernatant solution. A pale green solid was obtained after evacuating HF. No peak was observed in the X-ray powder photograph. No weight change was observed after the attempt to separate excess BiF$_5$ from the product by vacuum sublimation at ~100°C. The X-ray powder photograph of the sample after the sublimation gave no peaks.

In a separate experiment, PrF$_3$ (67 mg, 0.34 mmol) and BiF$_5$ (521 mg, 1.71 mmol) were interacted in HF (~2 cm$^3$) for ~20 hours at room temperature. X-ray powder diffraction of a solid obtained after evacuating HF detected only the unreacted BiF$_5$. The decrease of the weight by 71 mg (0.23 mmol as BiF$_3$) was observed after vacuum sublimation. The X-ray powder photograph of the sample after the sublimation gave no peaks, either.

PrF$_3$ + SbF$_5$

PrF$_3$ (100 mg, 0.505 mmol) was interacted with excess SbF$_5$ in HF (~2 cm$^3$) for ~20 hours at room temperature. PrF$_3$ completely dissolved in HF to give a green solution. A pale green solid was obtained after evacuating excess SbF$_5$ and HF. The weight uptake of the solid was 481 mg (2.22 mmol as SbF$_3$). X-ray diffraction of the solid showed a complex pattern different from that of PrF$_3$.

7.4 Discussion

Reactions of PrF$_3$ with fluorobases

PrF$_3$ does not react with monobasic metal fluorides (NaF, KF, CsF and AgF) in HF whereas double salts like MREF$_4$ and M$_3$REF$_6$ are formed in their melts[2]. The
solubility of REF_3 in HF is so low that the dissolution of REF_3 by forming RE(III)
species like REF_3 + 2^– does not occur at room temperature. The dissolution of REF_3 was
not observed even in a highly basic solution such as HF saturated with AgF. NaF,
KF, CsF and AgF react only with the solvent HF to form their bifluorides, M(HF)_n F.
Thus, REF_3 does not act as a fluoroacid in HF.

In contrast to the HF system, formation of compounds of REF_3 and NOF,
NOR_2F_7, NOREF_4 and (NO)_3REF_2F_4 has been reported in the NO_2-HF solution (NO_2 :
HF = 20 : 80 in mol%)[9]. In NO_2-HF system, NOF and HNO_3 are formed by the
following equilibrium[10]:

\[ \text{N}_2\text{O}_4 + \text{HF} \rightarrow \text{NOF} + \text{HNO}_3 \]  

The solubility of RE in this system has been reported to be 0.4 ~ 0.8 kg m\(^{-3}\) for Y, La, Ce,
Pr, Nd and Sm at 25°C[11]. It is not clear in this case whether REF_3 acts as a fluoroacid
or not since the compounds have not been characterized. However, the formation of the
compounds of NOF and REF_3 is considered to be promoted by the dissolution of REF_3 in
the solution.

**Reactions of REF_3 with fluoroacids**

REF_3 dissolves more or less in HF in the presence of fluoroacids. PrF_3 (pale green
solid) dissolves in HF with BF_3, BiF_5 and SbF_5 to give pale green solutions. The
solubility is larger in HF-BiF_5 and SbF_5 solutions than in HF-BF_3. REF_3 is considered to
act as a fluorobase under a highly acidic condition, for example;

\[ \text{REF}_3 + 3n\text{HF} \rightarrow \text{RE}^{3+}(\text{sol}) + 3(\text{HF})_n F^- \]  

NdF_3 (red purple solid) also dissolves in acidified HF. The dissolution of the colorless
heavy earth fluorides was not observed in the present study.

The formation of REF_3-BF_3 compounds where RE = Y, La, Cs, Pr, Nd, Sm, Eu,
Gd, Tb, Dy, Er and Yb was confirmed by gravimetry and X-ray powder diffraction (see
Table 7-2). The formation of REF_3-BF_3 compounds seems to be very slow probably due
to the low solubility of REF$_3$ in HF. The presence of REF$_3$ remained in some products is explained by incomplete reaction and/or the decomposition of the compounds during the pumping. Recently, Mazej et al. reported that a partial liberation of BF$_3$ and AsF$_5$ from the compounds of REF$_3$-BF$_3$ and REF$_3$-AsF$_5$ occurs under a dynamic vacuum at room temperature[12]. There is a tendency that free REF$_3$ is found in the product of heavy earth. For light earth series, free CeF$_3$ was exceptionally detected with the compound of BF$_3$. In the case of PrF$_3$-BF$_3$ system, the overnight interaction was not enough to complete the reaction, the unreacted PrF$_3$ being remained. The stability of the compound seems to decrease as the ionic radius of RE$^{3+}$ decreases. Fig. 7-1 shows the lattice enthalpy of REF$_3$ at 25°C represented by the following equation:

$$\text{REF}_3(s) \rightarrow \text{RE}^{3+}(g) + 3\text{F}^-(g) \quad \Delta H_L$$

(3)

The lattice enthalpy is calculated by a thermodynamic cycle combined with the enthalpy of formation of REF$_3$[13], RE$^{3+}$[14] and F$^-$ (= -247 kJ mol$^{-1}$[14]). There is almost linear

![Fig. 7-1 Dependence of the lattice enthalpy of REF$_3$ on the reciprocal ionic radius of RE$^{3+}$.](image-url)
relationship between $\Delta H_1$ and reciprocal ionic radius of RE$^{3+}$. Fluorobasicity of REF$_3$ generally decreases with the increase of $\Delta H_1$, the coulombic interaction between RE$^{3+}$ and F$^-$ being increased to stabilize REF$_3$.

HoF$_3$ and TmF$_3$ do not react with BF$_3$ in spite of the formation of that of YbF$_3$ which has a smaller ionic radius than they have. The reactivity of REF$_3$ with BF$_3$ in HF seems to be governed not only by thermodynamic but also kinetic factors. The starting REF$_3$'s prepared from their trichlorides are more 'reactive' than commercially supplied ones as seen in the results of EuF$_3$, TbF$_3$, ErF$_3$ and YbF$_3$. The difference might be explained by the kinetic reason caused by the difference in the crystallite sizes of REF$_3$ prepared from their trichlorides and that commercially supplied. The line widths in the X-ray powder patterns of REF$_3$'s (Fig. 7-2) prepared from their trichlorides are broader than

![Fig. 7-2 X-ray powder diffraction profiles of EuF$_3$'s prepared from EuCl$_3$ and commercially supplied.](image_url)
those of trifluorides commercially supplied. There is a possibility that all the REF₃'s including even the trifluorides of Ho, Tm and Lu react with BF₃ if they are prepared from their trichlorides and have lower crystallinity, which has not been proved yet.

For vacuum stable compounds, the molar ratios, BF₃ / REF₃, are listed in Table 7-2 assuming that the weight uptake of the sample after the reaction was caused only by BF₃. In the case of PrF₃, the ratio is ~2.3. When it is smaller than this value, the pattern of PrF₃ is observed in the X-ray powder photograph. The BF₃ / PrF₃ ratio of the product not containing free PrF₃ was also confirmed to be ~2.3 by ICP spectroscopy of praseodymium and boron. Fig. 7-3 summarizes the ratios of BF₃ / REF₃ of the products in which the REF₃-BF₃ compounds were detected by X-ray diffraction. The square marks in the plot represent the products not containing free REF₃ and the X marks denote the products with some free REF₃. There is a tendency that the ratio generally decreases with
decreasing the ionic radius of $\text{RE}^{3+}$. Anyway, roughly speaking, $\text{BF}_3 / \text{REF}_3$ ratios are around two. The ratios lower than two found in Y, Ce, Er and Yb might be explained by the decomposition during the pumping since the presence of free $\text{REF}_3$ is always found in the samples. The compositions of the compounds obtained by Mazej et al. [12] were classified into two groups; $\text{BF}_3 / \text{REF}_3 = 2$ for light earths and 1 for heavy earths. Their results differ from ours in the compositions of the compounds of heavy earths. However, neither the presence of free $\text{REF}_3$ nor the formation of the compound have been detected since their products are X-ray amorphous. Thus, the existence of the 1 : 1 compounds of $\text{REF}_3 - \text{BF}_3$ is still controversial.

The X-ray powder pattern of the compound of $\text{PrF}_3$ and $\text{BF}_3$ was indexed as an orthorhombic unit cell with the lattice parameters of $a_0 = 11.389$, $b_0 = 6.325$ and $c_0 = 6.869$ Å, as listed in Table 7-3. The possible space group, Pnc2 or Pnmc, is expected from the systematic extinction of the observed lines. The X-ray powder patterns of the compounds of $\text{REF}_3 - \text{BF}_3$ ($\text{RE} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Eu}, \text{and} \text{Gd}$) are isomorphic with that of $\text{PrF}_3 - \text{BF}_3$ compound. In Table 7-4, the lattice parameters of the isomorphic series are listed and Fig. 7-4 shows the relation between the cubic root of the lattice volume of the isomorphic series and the reciprocal ionic radius of $\text{RE}^{3+}$. The cubic root of the lattice volume almost linearly increases with the ionic radius of $\text{RE}^{3+}$. The X-ray powder patterns of the compounds of $\text{REF}_3 - \text{BF}_3$ ($\text{RE} = \text{Tb, Dy, Y, Er, and Yb}$) are not isomorphic with that of $\text{PrF}_3 - \text{BF}_3$. The crystal structures of the products are classified into, at least, three types: the structure of $\text{LaF}_3 - \text{BF}_3$, that of $\text{REF}_3 - \text{BF}_3$ ($\text{RE} = \text{Ce, Nd, Sm, Eu, and Gd}$), and that of $\text{REF}_3 - \text{BF}_3$ ($\text{RE} = \text{Tb, Dy, Y, Er, and Yb}$). The X-ray powder patterns of the last group are not confirmed to be isomorphic because only broad and weak lines were observed. The dependence of the cubic root of the lattice volume on the ionic radius of $\text{RE}^{3+}$ and the dissolution of the compound in acetonitrile ($\text{CH}_3\text{CN}$) at room temperature suggest that the compounds are ionic.
Table 7-3  X-ray powder diffraction pattern of PrF₃-BF₃ (orthorhombic, $a_0$=11.389 Å, $b_0$=6.325 Å, $c_0$=6.869 Å). Possible space group is Pnc2 or Pncm(Pmna).

<table>
<thead>
<tr>
<th>hkl</th>
<th>Int.</th>
<th>Obs.</th>
<th>Calc. $10^4 / d^2$ Å⁻²</th>
<th>hkl</th>
<th>Int.</th>
<th>Obs.</th>
<th>Calc. $10^4 / d^2$ Å⁻²</th>
</tr>
</thead>
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<td>730</td>
<td>m</td>
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Abbreviations used: s, strong; m, medium; w, weak; v, very.
Table 7-4  Lattice parameters of the isomorphous series of REF₃-BF₃ compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a₀ / \text{Å} )</th>
<th>(b₀ / \text{Å} )</th>
<th>(c₀ / \text{Å} )</th>
<th>(V / \text{Å}³ )</th>
</tr>
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<tr>
<td>CeF₃-BF₃</td>
<td>11.43</td>
<td>6.343</td>
<td>6.905</td>
<td>500.6</td>
</tr>
<tr>
<td>PrF₃-BF₃</td>
<td>11.39</td>
<td>6.325</td>
<td>6.869</td>
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</tr>
<tr>
<td>NdF₃-BF₃</td>
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<td>6.319</td>
<td>6.881</td>
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<tr>
<td>SmF₃-BF₃</td>
<td>11.28</td>
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<td>6.807</td>
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<tr>
<td>EuF₃-BF₃</td>
<td>11.18</td>
<td>6.225</td>
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</tr>
<tr>
<td>GdF₃-BF₃</td>
<td>11.28</td>
<td>6.209</td>
<td>6.761</td>
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</table>

Fig. 7-4  Dependence of the cubic root of the lattice volume of REF₃-BF₃ compounds on the ionic radius of RE³⁺.

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The IR spectra of REF₃-BF₃ compounds are shown in Fig. 7-5. The broad and split peaks around 1100 cm⁻¹ are assigned to the ν₃ mode of BF₄⁻ by comparing with the spectrum of NaBF₄ (also shown in Fig. 7-5) which contains discrete BF₄⁻ (Td). The splitting of the ν₃ mode in the spectra of REF₃-BF₃ would be explained by the strong interaction of the fluorine atoms in BF₄ units with rare earth atom. This might be explained by the formation of a large complex cation like RE(FBF₃)₆³⁺. A complex cation of RE(III) coordinated by SO₂ have been reported in [RE(SO₃)ₓ(AsF₆)₂]⁺AsF₆⁻ prepared in SO₂ solvent[15]. The similarity in the spectra of the compounds of PrF₃ and SmF₃ also supports that their structures are closely related with each other. The spectra of the compounds of LaF₃, DyF₃ and YF₃ are obviously different from those of the isomorphous series reflecting the differences in their structures.

The reactions of PrF₃ with SbF₅ and BiF₅ also gave stable compounds. The ratios of BiF₅ / PrF₃ and SbF₅ / PrF₃ were 3.03 - 4.26 and 4.40, respectively. The complex pattern was obtained for the product of PrF₃ and SbF₅, while only a few weak peaks were observed for the product of PrF₃ and BiF₅. The formation of the X-ray amorphous phases has been also reported in the compounds of REF₃ with BF₃ and AsF₅[8]. The stoichiometry of these compounds are again not straightforward as is expected from the formal ionic charge balances of RE³⁺, MF₆⁻ and M₂F₁₁⁻ (M = Bi and Sb).

Figure 7-6 shows the IR spectra of BiF₅ and the compound of PrF₃ and BiF₅. The peak around 620 cm⁻¹ is assigned to ν₃ mode of BiF₆ unit with O₅ symmetry. BiF₅ has a tetragonal α-UF₅ structure in which a trans-linked chain of BiF₆ octahedra via fluorine bridging bonds exists along c-axis[16]. The close frequency of ν₃ mode for PrF₃-BiF₅ compound to that of BiF₅ suggests that the former does not contain discrete BiF₆⁻ anions but fluorine-bridged structures such as (-FBiF₅)ₓ or (-Pr-F-BiF₅) since the ν₃ mode of discrete BiF₆⁻ anion appears at lower frequency, for example, around 570 cm⁻¹ as seen in CsBiF₆[17].

Compared with the compounds of PrF₃ and BiF₅, the IR spectrum of the compound
Fig. 7-5  IR spectra of the compounds of REF₃ and BF₃. The spectrum of NaBF₄ is also shown for comparison.
of SbF$_5$ is more complex as shown in Fig. 7-7. The groups of peaks around 650 ~ 750 and 500 ~ 550 cm$^{-1}$ are ascribed to the Sb-F(terminal) and Sb-F(bridging) stretching bands, respectively, by comparison with the spectra of [Re$_2$F$_9$O$_2$][Sb$_{11}$]$_2$[18], UO$_2$F$_2$.3SbF$_5$[19], UO$_2$F$_2$.4SbF$_5$[20] and so on. Thus, this compound probably contains fluorine-bridged structures such as Sb$_{11}$F$_{14}^-$, (-FSbF$_5$)$_n$ and Pr-F-SbF$_5$ units.
Fig. 7-7. IR spectrum of the compound of PrF$_3$ and SbF$_5$. 
References

CHAPTER 8

Acid-base reactions of rare earth trichlorides in molten LiCl-KCl eutectic

8.1 Introduction

Rare earth (RE) elements are important for syntheses of various functional materials having unique catalytic and magnetic properties. The electrochemical process in molten alkaline halides is one of the strong candidates to synthesize such materials because of their wide electrochemical windows. The electrochemical syntheses of some alloys containing rare earth elements have been investigated in LiCl-KCl eutectic melt to control the bulk or surface composition[1,2]. These chlorides are hygroscopic and the perfect elimination of oxide species from a considerable amount of melt is technically difficult, which sometimes causes the precipitation of the oxides (RE₂O₃) or oxide chlorides (REOCl). The precipitation of the compounds occasionally affects electrochemical measurements in molten chlorides.

REOCl is easily formed by heating hydrated RECl₃ in air at around 300°C[3]. Under this condition, the formation of RE₂O₃ does not occur. Therefore, it has been considered that REOCl is dominantly formed in rare earth molten chlorides contaminated by O²⁻. Picard et al. studied the stabilities of REOCl and RE₂O₃ for some rare earth elements (La, Ce, Pr, Nd, Gd and Y) in LiCl-KCl eutectic[4]. They showed that formation of RE₂O₃ for Pr, Nd and Gd occurs at higher oxide ion concentration and only Y₂O₃ precipitates regardless of the oxide ion concentration. However, the available thermodynamic data of REOCl's are not comprehensive, especially those of heavy rare earths, compared to those of RE₂O₃’s and RECl₃’s and the thermodynamic explanation

for formation of the precipitates has not been made systematically in this system.

In this chapter, identification of the precipitates was carried out in LiCl-KCl eutectic containing RECl₃ at several O²⁻ concentrations including 'zero' at 450°C. The thermodynamic data of REOCl at high temperatures are estimated and applied to LiCl-KCl eutectic containing RE(III) and O²⁻ to predict the precipitates to be formed in the melts.

8.2 Experimental

Materials

All the reagents were handled in a glove box of Ar atmosphere. LiCl and KCl (Wako Chemicals, purity 99.0 and 99.9%, respectively) were dried in Pyrex glass ampoules under vacuum elevating the temperature to 200°C and holding it for several hours until the pressure becomes below 10⁻³ Torr. They were transferred into the glove box and mixed (eutectic composition, LiCl : KCl = 59 : 41 in molar fraction). Li₂O (Mitsuwa’s Chemicals, purity 95%) was dried under vacuum and heated up to 550°C to decompose the trace amount of LiOH to Li₂O. Anhydrous RECl₃’s were prepared from RECl₃·6H₂O’s (Wako Chemicals, purity 99.5% or more). They were carefully dehydrated under vacuum at lower temperatures less than 200°C and heated up to ~300°C with the intermittent treatment with dry HCl to convert contaminated REOCl to RECl₃. X-ray powder diffraction detected no impurities in the prepared samples.

Preparation and identification of the precipitates

The composition of RECl₃ in LiCl-KCl eutectic, 1 or 3 mol%, was chosen because the identification of the precipitates in LiCl-KCl becomes difficult by X-ray diffraction below this composition. The temperature was fixed to 450°C for all the experiments. The melting point of LiCl-KCl eutectic is 353°C and 450°C is often chosen as a reaction temperature for electrochemical measurements because Pyrex glass is stable and the
vaporization of LiCl is negligible.

LiCl-KCl eutectic, RECl₃ (1 or 3 mol%) and Li₂O (1 or 3 mol%, pO²⁻ < 2) were mixed and loaded in a Pyrex glass reaction tube connected to a Whitey stainless steel valve. The tube was connected to a vacuum line to keep the ambient pressure of Ar in the tube. The temperature was elevated to 450°C by a transparent electric furnace to observe the melting of the mixture and the formation of precipitate. After holding the temperature for several hours, the tube was cooled and transferred to the glove box. The precipitate was collected from the cooled melts and charged in a quartz glass capillary to prepare the sample for X-ray powder diffraction. Experiments without Li₂O were carried out to examine the precipitates from the melt not containing O²⁻.

8.3 Results and discussion

8.3.1 The precipitates in the absence of oxide ion

The addition of 3 mol% of LaCl₃ and NdCl₃ to LiCl-KCl eutectic at 450°C gives clear colorless and purple melts, respectively. The addition of 1 mol% of GdCl₃ gives a clear colorless melt, the precipitate being formed when it is increased to 3 mol%. The addition of 1 mol% of YCl₃ and YbCl₃ gives the formation of precipitates in the melts. The precipitates are found to be the 3 : 1 compounds of KCl and RECl₃, K₃RECl₆ (RE = Gd, Y and Yb)[5]. Neither the formation of RE₂O₃ nor REOCl was observed in all the experiments.

The formation of K₃RECl₆'s has been reported in KCl-RECl₃ systems[5], their X-ray powder patterns having not been indexed yet. In this investigation, the X-ray powder pattern of α-K₃YCl₆ (low temperature form, a phase transition occurring in the cooling process.) is indexed as a simple cubic cell with the lattice parameter, \( a₀ = 10.55 \text{ Å} \) and \( Z = 4 \) as shown in Table 8-1. The X-ray powder patterns of K₃RECl₆ for Gd and Yb are isomorphous, their lattice parameters, \( a₀ \), being 10.65 and 10.53 Å, respectively. In the
Table 8-1  X-ray powder pattern of α-K₃YCl₆. The index was made as a simple cubic unit cell with the lattice parameter, \( a_0 = 10.55 \text{ Å} \).

<table>
<thead>
<tr>
<th>Intensity</th>
<th>( d_{\text{obs}} ) / Å</th>
<th>( d_{\text{calc}} ) / Å</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>5.998</td>
<td>6.091</td>
<td>111</td>
</tr>
<tr>
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<td>5.275</td>
<td>200</td>
</tr>
<tr>
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<td>3.730</td>
<td>220</td>
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<tr>
<td>w</td>
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<td>3.336</td>
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</tr>
<tr>
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<td>2.926</td>
<td>320</td>
</tr>
<tr>
<td>vw</td>
<td>2.819</td>
<td>2.820</td>
<td>321</td>
</tr>
<tr>
<td>s</td>
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<td>2.638</td>
<td>400</td>
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<td>2.487</td>
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</tr>
<tr>
<td>w</td>
<td>2.430</td>
<td>2.420</td>
<td>331</td>
</tr>
<tr>
<td>s</td>
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<td>2.154</td>
<td>422</td>
</tr>
<tr>
<td>w</td>
<td>2.028</td>
<td>2.030</td>
<td>333, 511</td>
</tr>
</tbody>
</table>

Abbreviations used: s, strong; m, medium; w, weak; v, very.

crystal structure of the related compound, Cs₂NaBkCl₆ (cubic, \( a_0 = 10.8050 \text{ Å} \)) [6], the bond length between Bk(III) and Cl⁻ corresponds to the sum of the ionic radii of Bk(III) and Cl⁻. It is strongly suggested that K₃RECl₆ is also a double salt rather than a complex salts containing a discrete anion, such as RECl₆⁻.

It seems that the precipitation of K₃RECl₆ is more likely to occur as the ionic radius of RE³⁺ decreases by lanthanide contraction which causes the increase of the coulomb interaction between RE³⁺ and Cl⁻.

8.3.2 The precipitates in the presence of oxide ion

When 3 mol% of Li₂O is added to LiCl-KCl eutectic containing 3 mol% of RECl₃ (RE = La and Nd), REOCl is precipitated. In the melt containing 1 mol% of Li₂O and RECl₃ (RE = Y, Yb), the precipitation of RE₂O₃ is observed. When a small amount of Li₂O (~0.5 mol%) is added to the melt containing 1 mol% of GdCl₃, the precipitation of GdOCl is observed. Further addition of Li₂O (~1 mol%) gives the precipitation of both Gd₂O₃ and GdOCl.
The formation of \( \text{RE}_2\text{O}_3 \) or \( \text{REOCl} \) in these melts is reasonably explained from the potential-pO\(^{2-}\) diagrams. In order to construct the potential-pO\(^{2-}\) diagrams, the RE(III)/RE(0) standard electrode potentials and the standard chemical potential of O\(^{2-}\) in LiCl-KCl eutectic at 450°C are required in addition to the free enthalpies of formation of \( \text{RECl}_3 \), \( \text{RE}_2\text{O}_3 \) and \( \text{REOCl} \) (see Appendix). The RE(III)/RE(0) standard electrode potentials are literally available only for La, Ce, Pr, Nd, Gd and Y\( \{4,7,8\} \). The standard chemical potential of the O\(^{2-}\) was estimated by the measurements of the solubility of some metal oxides (ZnO, CoO, MgO, FeO, NiO, UO\(_2\), UO\(_2\), PdO, Bi\(_2\)O\(_3\)) in LiCl-KCl eutectic at 450°C\( \{9,10\} \), which was employed for the calculation here:

\[
\frac{\mu^0(\text{O}^{2-})}{2.303RT} = 9.3 \quad \text{(in molar fraction)}
\]  

(1)

Only the following redox equilibria are taken into account in LiCl-KCl eutectic containing the trivalent rare earth species, RE(III), and O\(^{2-}\) because at this temperature the formation of divalent species can be ignored for La, Gd and Y:

\[
\text{RE(III)} + 3e^- = \text{RE}(0) \quad \text{(i)}
\]

\[
\text{RE}_2\text{O}_3 + 6e^- = 2\text{RE}(0) + 3\text{O}^{2-} \quad \text{(ii)}
\]

\[
\text{REOCl} + 3e^- = \text{RE}(0) + \text{O}^{2-} + \text{Cl}^- \quad \text{(iii)}
\]

For these equilibria, the potential against Cl\(_2\)/Cl\(^-\) electrode are expressed as follows;

\[
E = E^0_{\text{RE(III)/RE}} + \frac{2.303RT}{3F} \log X_{\text{RE(III)}} \quad \text{(2)}
\]

\[
E = \frac{\Delta G_i(\text{REOCl})}{3F} - \frac{\mu^0(\text{O}^{2-})}{3F} + \frac{2.303RT}{3F} p\text{O}^{2-} \quad \text{(3)}
\]

\[
E = \frac{\Delta G_i(\text{RE}_2\text{O}_3)}{6F} - \frac{\mu^0(\text{O}^{2-})}{2F} + \frac{2.303RT}{2F} p\text{O}^{2-} \quad \text{(4)}
\]

where \( X_{\text{RE(III)}} \) is the concentration of trivalent rare earth elements in molar fraction and \( p\text{O}^{2-} \) represents the logarithmic concentration of O\(^{2-}\) in molar fraction defined as:

\[
p\text{O}^{2-} = -\log X_{\text{O}^{2-}}.
\]

(5)

The potentials in eqs. (3) and (4) depend linearly on \( p\text{O}^{2-} \). Although the absolute value of \( \mu^0(\text{O}^{2-}) \) is still controversial, it does not affect the comparison of the relative stability of \( \text{REOCl} \) to \( \text{RE}_2\text{O}_3 \).
Fig. 8-1 Potential-pO$_2^-$ diagrams for (a) lanthanum, (b) gadolinium and (c) yttrium in LiCl-KCl eutectic at 450°C. The concentrations of RE(III) and O$_2^-$ are given in molar fraction.
Figure 8-1 shows typical examples of the potential-pO²⁻ diagrams for La, Gd and Y systems. The concentration of RECl₃ in LiCl-KCl eutectic is chosen to be 1 mol%. Since LaOCl is thermodynamically more stable than La₂O₃ at 450°C, LaOCl selectively precipitates in the melt containing O²⁻ (a), which agrees with the result of the previous workers [4]. On the other hand, only Y₂O₃ is formed because the relative stability of Y₂O₃ to YOCl is reversed in this case (b). In LiCl-KCl-GdCl₃ system, the formation of Gd₂O₃ is preferred in the lower pO²⁻ region. But the precipitation of GdOCl becomes favorable as pO²⁻ increases because the relative stability of Gd₂O₃ against GdOCl is reversed at pO²⁻ = 2 (c).

To judge whether the formation of RE₂O₃ or REOCl occurs for each element, the relative stability of RE₂O₃ against REOCl was estimated in terms of the free enthalpy change of the following reaction;

\[ \text{REOCl} + \frac{1}{2} \text{O}^{2-} = \frac{1}{2} \text{RE}_2\text{O}_3 + \text{Cl}^- \]  \hspace{1cm} (iv)

\[ \Delta G = \frac{1}{2} \Delta G({\text{RE}_2\text{O}_3}) - \Delta G({\text{REOCl}}) - \frac{1}{2} \mu^0(\text{O}^{2-}) + \frac{2.303RT}{2} \text{pO}^{2-} \]  \hspace{1cm} (6)

Figure 8-2 shows the plot of \( \Delta G \) against the reciprocal ionic radii of rare earth elements when pO²⁻ = 2 at 450°C. The tendency is that the formation of RE₂O₃ becomes more favorable than that of REOCl as the ionic radius of RE³⁺[11] is decreased except in the case of Yb. The stability of RE₂O₃ to REOCl is comparable around the ionic radius of Gd³⁺. The formation of RE₂O₃ and REOCl is considered to be sensitive to the concentration of O²⁻ for the elements lying near the zero line in the plot.

The values of \( \Delta G \) for reaction (iv) are considered to be governed by the difference in the formation enthalpies of REOCl and RE₂O₃ if the entropy changes of reaction (iv) are similar for all the elements. Because both REOCl and RE₂O₃ are ionic compounds, the difference in their formation enthalpies is attributed to the difference in the lattice energies of RE₂O₃ and REOCl. This coincides with the observation that, except for a few heavier rare earths, \( \Delta G \) shows a roughly linear correlation with the reciprocal ionic radius of RE³⁺.
It should be noted that the heating of all the hydrated RECl₃ in air at 450°C always gives REOCl₃, which would be explained by slow kinetics of the oxidation in the solid state compared to that in melts of heavy earth chlorides.

8.3.3 Dehydration of rare earth trichloride hydrates

Except LaCl₃, anhydrous RECl₃ cannot be prepared by the thermal dehydration of hydrated RECl₃, the formation of REOCl being unavoidable even in the inert gas. Figure 8-3 shows the logarithms of equilibrium constants of the hydrolysis of RECl₃[12,13,14, 15,16], log $K_{\text{Hyd}}$, for some rare earth elements at 100, 200 and 300°C. At 100°C, the formation of REOCl is negligible for all the rare earth elements. Even at 200°C, for light

Fig. 8-2 Dependence of the free enthalpy changes, $\Delta G$, of the reaction;

$$\text{REOCl} + \frac{1}{2} \text{O}^{2-} = \frac{1}{2} \text{RE}_2\text{O}_3 + \text{Cl}^-$$

on the reciprocal ionic radii of RE³⁺ in LiCl-KCl eutectic when pO²⁻ = 2 at 450°C.
earth, the hydrolytic formation of REOCl is still unfavorable. However, on the other hand, the dehydration is considered not to be complete because RECl₃·H₂O is rather stable kinetically and not dehydrated unless the temperature exceeds ~300°C[3]. At 300°C, pure anhydrous LaCl₃ would be formed by thermal dehydration while the formation of REOCl occurs to a greater or lesser degree for other heavier rare earths in the same condition. In the case of Ho, Y and Tm, REOCl would be the major product. Therefore, the dehydration of hydrated heavy earth trichlorides, including Y, to obtain anhydrides should be carried out at temperatures below 200°C to minimize the formation of REOCl, followed by heating gradually to ~300°C with intermittent treatment of dry HCl and
elimination of $\text{H}_2\text{O}$ from the system. Since the rate of conversion of $\text{REOCl}_3$ to $\text{RECl}_3$ seems to be very slow in solid-gas reaction, it is difficult to obtain pure anhydrous $\text{RECl}_3$ from the reagents containing a large amount of $\text{REOCl}$ formed by hydrolysis.

### 8.4 Estimation of $\Delta G_r(\text{REOCl})$ at 450°C (723K)

Since the formation enthalpies of $\text{REOCl}$ are not literally available, the estimation was made in the following manner.

The reaction thermodynamics of the hydrolysis of some $\text{RECl}_3$'s ($\text{RE} = \text{La, Ce, Pr, Nd, Sm, Gd, Tb, Y, Er and Tm}$) have been studied by several workers[12,13,14,15,16]:

$$\text{RECl}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) = \text{REOCI}(\text{s}) + 2\text{HCl}(\text{g})$$  \hspace{1cm} (v)

$\Delta C_p$, for reaction (v) was estimated for La[12].

$$\Delta C_p = -12 - 1.5 \times 10^{-3} T + \frac{1.8 \times 10^{-5}}{T} \hspace{1cm} \text{(in J K}^{-1})$$  \hspace{1cm} (8)

Assuming $\Delta C_p$'s for other rare earth elements are the same, the free enthalpy changes, $\Delta G_{\text{hyd}}$, is given by:

$$\Delta G_{\text{hyd}} = H_0 + 2.7 \times 10^{-2} T \log T + 7.5 \times 10^{-6} T^2 - \frac{92}{T} + I \times 10^{-3} T$$  \hspace{1cm} \text{(in kJ).} \hspace{1cm} (9)

The constants, $H_0$ and $I$, were re-calculated in this study from the equilibrium constants reported in refs 12-16 by means of the weighed least-square refinement. The errors in $H_0$ and $I$ are estimated at 1.6% or less for all the elements. Then the enthalpy changes, $\Delta H_{\text{hyd}}$, and the entropy changes, $\Delta S_{\text{hyd}}$, of reaction (v) are calculated from the following equations:

$$\Delta H_{\text{hyd}} = H_0 + \int_0^T \Delta C_p dt$$

$$= H_0 - 1.2 \times 10^{-2} T - 7.5 \times 10^{-7} T^2 - \frac{1.8 \times 10^2}{T}$$  \hspace{1cm} \text{(in kJ)} \hspace{1cm} (10)

$$\Delta S_{\text{hyd}} = \frac{\Delta H_{\text{hyd}} - \Delta G_{\text{hyd}}}{T}$$

$$= -12 (1 + \ln T) - 1.5 \times 10^{-3} T - \frac{9.2 \times 10^4}{T^2} + I$$  \hspace{1cm} \text{(in J K}^{-1}) \hspace{1cm} (11)
The difference in $\Delta H_{n,d}$ is attributed to the difference in the formation enthalpies of $\text{RECl}_3$ and $\text{REOCl}$, $\Delta H_f(\text{REOCl})$ and $\Delta H_f(\text{RECl}_3)$, respectively. Since $\text{REOCl}$ is an ionic compound, $\Delta H_f(\text{REOCl})$ is written as eq. (12):

$$\Delta H_f(\text{REOCl}) = \Delta H_f(\text{RECl}_3) - \Delta H_f(\text{RE}^{3+}) - \Delta H_f(\text{O}^{2-}) - \Delta H_f(\text{Cl}^-)$$  \hspace{1cm} (12)

where $\Delta H_f(\text{RE}^{3+})$, $\Delta H_f(\text{O}^{2-})$ and $\Delta H_f(\text{Cl}^-)$ are the formation enthalpies of gaseous $\text{RE}^{3+}$, $\text{O}^{2-}$ and $\text{Cl}^-$, respectively and $\Delta H_f(\text{REOCl})$ is the lattice energy of $\text{REOCl}$. As $\text{RECl}_3$ is also an ionic solid, $\Delta H_f(\text{RECl}_3)$ is given by;

$$\Delta H_f(\text{RECl}_3) = \Delta H_f(\text{RECl}_3) - \Delta H_f(\text{RE}^{3+}) - 3 \Delta H_f(\text{Cl}^-).$$  \hspace{1cm} (13)

From eqs. (12) and (13), the difference of $\Delta H_f$ of $\text{REOCl}$ and $\text{RECl}_3$, $\Delta \Delta H_f$ is given by;

$$\Delta \Delta H_f = \Delta H_f(\text{REOCl}) - \Delta H_f(\text{RECl}_3)$$

$$= [\Delta H_f(\text{REOCl}) - \Delta H_f(\text{RECl}_3)] - \Delta H_f(\text{O}^{2-}) + 2 \Delta H_f(\text{Cl}^-).$$  \hspace{1cm} (14)

![Fig. 8-4](image_url)

**Fig. 8-4** Dependence of the reciprocal cube roots of the formula volumes, $1/\sqrt[3]{V}$, of $\text{REOCl}$ on the reciprocal ionic radii of $\text{RE}^{3+}$.
Since the last two terms are independent of the metals, $\Delta H_{byd}$ depends only on the difference between $\Delta H_L(\text{RECl}_3)$ and $\Delta H_L(\text{REOCl})$.

The crystal structures of REOCl are the same regardless of the metals, i.e., a tetragonal PbClF-type[17]. On the other hand, the crystal structures of RECl$_3$ are classified into three types; hexagonal UCl$_3$-type for La to Gd, orthorhombic PuBr$_3$-type for Tb and monoclinic AlCl$_3$-type for Dy to Lu and Y[17]. The influences of the difference in the crystal structures of RECl$_3$ to $\Delta H_{byd}$ and $\Delta S_{byd}$ should be checked.

Figure 8-4 shows the plots of the reciprocal cube roots of the formula volumes, $1/\sqrt[3]{v}$, of REOCl, versus the reciprocal ionic radii or RE$^{3+}$. The $\Delta H_L(\text{REOCl})$ is considered to depend linearly on $1/\sqrt[3]{v}$ of REOCl. Since the crystal structures of REOCl are all the same, the plot shows the linear correlation between $1/\sqrt[3]{v}$ of REOCl, i.e. $\Delta H_L(\text{REOCl})$, and the reciprocal ionic radii of RE$^{3+}$. Figure 8-5 shows the lattice energies of

![Lattice Energy Diagram](image)

Fig. 8-5 Dependence of the calculated lattice energies of RECl$_3$ on the reciprocal ionic radii of RE$^{3+}$ at 25°C (BFHC = Born-Fajans-Haber Cycle).
RECl$_3$ at 25°C[11] against the reciprocal ionic radii of RE$^{3+}$. Although the three types of crystal structures of RECl$_3$ exist, there is also a good linear relationship between $\Delta H_L$ (RECl$_3$) and the reciprocal ionic radii of RE$^{3+}$ at 25°C. Thus the difference in the crystal structures of RECl$_3$ does not affect the dependence of $\Delta H_{byd}$ on the reciprocal ionic radii of RE$^{3+}$ as shown in Fig. 8-6. By inter- and extrapolating the line, the $\Delta H_{byd}$ at 450°C (723K) for Ce, Pm, Eu, Dy, Ho, Yb and Lu are estimated as listed in Table 8-2.

In Table 8-2, the values of $\Delta S_{byd}$ are similar for La to Gd, $\sim$130 J K$^{-1}$, and for Er to Tm, $\sim$110 J K$^{-1}$. This difference would be caused by the difference in the crystal structures of RECl$_3$. Therefore, the average values of $\Delta S_{byd}$ for La to Gd are applied to Ce, Pm and Eu, and the average values of $\Delta S_{byd}$ for Y, Er and Tm are employed to Dy, Ho, Yb and Lu. Although yttrium is one of the light earths in terms of atomic weight, it should be classified as a heavy rare earth in the sense of its chemical properties. The values of

![Graph](image-url)

Fig. 8-6  Dependence of the enthalpy changes of the hydrolysis of RECl$_3$ on the reciprocal ionic radii of RE$^{3+}$ at 450°C.
\( \Delta G_{\text{hyd}} \) are also shown in Table 8-2.

Based on these calculations, the free enthalpy changes of formation, \( \Delta G_f^{723} \), the formation enthalpies, \( \Delta H_f^{723} \) and the entropies, \( S_f^{723} \), of REOCI at 450°C (723K) are obtained by combining with those of RECl₃, H₂O and HCl at this temperature[18]. Some \( \Delta G_f^{723} \) are not listed in Table 8-2 since the values of \( \Delta G_f(\text{RECl}_3) \) are not literally available.

Table 8-2  Thermodynamic data of the hydrolysis reaction of RECl₃ and those of REOCI at 450°C (723K). The values with asterisks(*) are extra- or interpolated from the other data.

<table>
<thead>
<tr>
<th>RE</th>
<th>( r_{\text{RE}^3-} )</th>
<th>( \Delta G_{\text{hyd}}^{723} ) kJ</th>
<th>( \Delta H_{\text{hyd}}^{723} ) kJ</th>
<th>( \Delta S_{\text{hyd}}^{723} ) J K⁻¹</th>
<th>( \Delta G_f^{723} ) kJ mol⁻¹</th>
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CHAPTER 9

General conclusion

A study was made to clarify acid-base reactions of halides and oxide halides in anhydrous hydrogen fluoride (HF) and LiCl-KCl eutectic melt. For this purpose, the reactions were carried out in extremely "dry" system described in Chapter 2. Reactions were discussed mainly based on the results obtained by characterization of the salts with the aid of structural and spectroscopic analyses.

In Chapter 3, the complex salts of silver(I) fluoride (AgF) and tungsten oxide tetrafluoride (WOF₄), AgWOF₅ and AgW₂O₂F₉, were obtained. The former was able to be prepared by shifting the following solvolysis equilibrium:

\[ 2\text{AgWOF}_5 + n\text{HF} \rightleftharpoons \text{Ag(HF)}_n\text{F} + \text{AgW}_2\text{O}_2\text{F}_9 \]  (1)

The complex anions, WOF₅⁻ and W₂O₂F₉⁻ were identified in the compounds by vibrational spectroscopy. The reaction of silver(II) fluoride (AgF₂) and WOF₄ gave only a 1 : 2 compound, AgFW₂O₂F₉, containing a W₂O₂F₉⁻ anion as follows:

\[ \text{AgF}_2 + 2\text{WOF}_4 \rightarrow \text{AgFW}_2\text{O}_2\text{F}_9 \]  (2)

This compound was also prepared by the reaction of AgW₂O₂F₉ with F₂:

\[ \text{AgW}_2\text{O}_2\text{F}_9 + 1/2 \text{F}_2 \rightarrow \text{AgFW}_2\text{O}_2\text{F}_9 \]  (3)

The fluoride ion affinity of WOF₄ by forming W₂O₂F₉⁻ anion is larger than that by forming WOF₅⁻. The oxidizing ability of AgFW₂O₂F₉ is so strong that xenon (Xe) is oxidized to Xe(II) giving XeF₂. WOF₄ according to the following equation:

\[ 5\text{AgFW}_2\text{O}_2\text{F}_9 + 2\text{Xe} \rightarrow 2\text{XeF}_2\text{WOF}_4 + 4\text{AgW}_2\text{O}_2\text{F}_9 + \text{AgF}_2 \]  (4)

Chapter 4 revealed the oxidizing ability of uranium hexafluoride (UF₆). The reaction of AgF and UF₆ resulted in formation of AgF₂ and AgUF₄. Formation of an intermediate complex salt, Ag₂UF₉, was detected by X-ray powder diffraction. A cubic structure of
Ag$_2$UF$_8$ was proposed and it was suggested that the oxidation of Ag(I) to Ag(II) would occur through ligand-bridged (inner sphere) mechanism in which “active complex,” (Ag-F-)$_2$UF$_6$, rearranges to AgF$_2$ and AgUF$_6$. Therefore, the overall reaction of AgF and UF$_6$ is represented as follows:

$$2\text{AgF} + \text{UF}_6 \rightarrow (\text{AgF}_2)_\text{UF}_6 \rightarrow \text{AgF}_2 + \text{AgUF}_6$$ (5)

In Chapters 5 and 6, the properties of uranyl fluoride (UO$_2$F$_2$) as a fluoroacid and fluorobase were examined in HF. In Chapter 5, the formation of the complex salts of univalent metal fluorides (MF, M = K, Cs and Ag) was studied. Especially, the new complex salt of AgF and UO$_2$F$_2$, AgUO$_2$F$_3$, was prepared by the following reaction in HF:

$$\text{AgF} + \text{UO}_2\text{F}_2 \rightarrow \text{AgUO}_2\text{F}_3$$ (6)

The compound was characterized by X-ray powder diffraction and vibrational spectroscopy, the existence of a new oxofluoroanion being suggested in AgUO$_2$F$_3$. The fluoroacidity of UO$_2$F$_2$ in HF was concluded to be very weak, comparable to that of HF. Chapter 6 is concerned to the properties of UO$_2$F$_2$ as a fluorobase in HF based on the reactions with fluoroacids. The fluorobasicity of UO$_2$F$_2$ was concluded to be very weak not acting as a fluorobase in the reactions with fluoroacids the fluoride ion affinities of which are higher than that of AsF$_5$. The compound of UO$_2$F$_2$ and AsF$_5$ was stable only at low temperatures, at least, below -78°C. A new complex salt of UO$_2$F$_2$ and BiF$_5$, UO$_2$F$_2$.2BiF$_5$, was prepared and characterized:

$$\text{UO}_2\text{F}_2 + 2\text{BiF}_5 \rightarrow \text{UO}_2\text{F}_2.2\text{BiF}_5$$ (7)

The structural similarities of UO$_2$F$_2$.2BiF$_5$ to UO$_2$F$_2$.2SbF$_5$ were suggested by X-ray powder diffraction and vibrational spectroscopy. The attempts at the preparation of the mixed valence compound, U$_2$O$_2$F$_7$, from UO$_2$F$_2$ and UF$_5$ which occurs in their melt failed due to the stability of UO$_2$F$_2$ having very low activities of acting as both fluoroacid and fluorobase in HF at room temperature.
In Chapter 7, behaviors of rare earth trifluorides (REF₃) as fluorobase and acid were studied. The reactions of REF₃ and univalent metal fluorides (MF, \(M = \text{Na, K, Cs and Ag}\)) gave no compounds, indicating the low fluoroacidity of REF₃ in HF at room temperature. The formation of the compounds of REF₃ and BF₃, BiF₃ and SbF₃ showed that REF₃ acts as a fluorobase in acidic conditions. The compounds of REF₃ and BF₃ for most of RE's were prepared:

\[
\text{REF}_3 + n\text{BF}_3 \rightarrow \text{REF}_3n\text{BF}_3 \quad (n = 2)
\]

(8)

The isomorphous series of the compounds were discovered from Ce to Gd having orthorhombic unit cells with a space group of \(Pnc2\) or \(Pnem\). The formation of the compounds of REF₃ and BiF₃ was confirmed, but the detailed properties of them have not been clarified yet.

Chapter 8 clarified the conditions of the formation of rare earth oxides (\(\text{RE}_2\text{O}_3\)) and oxide chlorides (REOCI) in LiCl-KCl eutectic melt (450°C) in the presence of oxide ion. Some thermodynamic parameters of REOCI at this temperature were estimated from the data of hydrolysis of the chlorides (RECl₃) taking account of the variation of the crystal structures of RECl₃ and REOCI with the ionic radius of \(\text{RE}^{3+}\). A tendency that formation of \(\text{RE}_2\text{O}_3\) becomes more favorable than that of REOCI as the decrease of the ionic radius of \(\text{RE}^{3+}\) was thermodynamically predicted and proved by experiments. The stability of \(\text{RE}_2\text{O}_3\) and REOCI is comparable for middle earths. In this chapter, the chemical behaviors of RECl₃ in the melt were determined also in the absence of oxide ion. The formation of a double salt of RECl₃ and KCl, \(K_3\text{RECl}_6\), was confirmed in the absence of oxide ion in the melt. The solubility of RECl₃ in the melt is lower for heavy earths than for light earths, resulting in the precipitation of \(K_3\text{RECl}_6\), since the stability of \(K_3\text{RECl}_6\) increases as the ionic radius of \(\text{RE}^{3+}\) decreases.
APPENDIX

Preparation of some reagents

This part describes detailed methods to prepare reagents used in this study. In every preparation method, care must be paid when anhydrous hydrogen fluoride (HF), hydrofluoric acid, fluorine (F₂) and other corrosive gases are used.

A.1 Preparation of silver fluoride (AgF)

Several synthetic methods were tried to prepare anhydrous AgF. The reaction of argentus oxide (Ag₂O, Wako Chemicals, purity 99% or more) with hydrofluoric acid (Nakarai Tesque, 47 vol%, guaranteed reagent grade) is the most effective way to prepare a large amount of AgF:

\[
\text{Ag}_2\text{O} + 2\text{HF} \rightarrow 2\text{AgF} + \text{H}_2\text{O}
\]  

(1)

\(\text{Ag}_2\text{O}\) was put in a PTFE beaker and 47 vol% hydrofluoric acid was poured on it. \(\text{Ag}_2\text{O}\) was readily dissolved, giving a clear solution with a trace of black precipitate. The precipitate was not dissolved even in the excess hydrofluoric acid, indicating that it was not \(\text{Ag}_2\text{O}\). The solution was filtered by a Teflon filter paper or decanted to eliminate the black precipitate. The solution was heated to 80 - 100°C in a fume hood to evaporate hydrofluoric acid solution and recrystallize AgF. The evaporation was repeated several times with addition of a small amount of hydrofluoric acid to avoid contamination of \(\text{Ag}_2\text{O}\). AgF solid was obtained as a lump which was unable to be powdered. The solid was crashed into small pieces and put in a Pyrex glass reactor for vacuum drying. The solid was heated at 100 - 200°C for several hours until the pressure above the solid becomes less than \(10^{-3}\) torr. No lines corresponding to other than AgF were detected by X-ray powder diffraction although a small amount of black particles was seen in the sample.
The reaction of Ag₂O with anhydrous HF was a convenient way to prepare a small amount of AgF (less than ~1g) without further vacuum drying. Ag₂O was put in one arm (Tube A) of a T-shaped FEP reactor (1/2" o.d.) and a large excess amount of HF was condensed on it. Ag₂O reacted readily with HF (even when gaseous HF was introduced in the reactor) evolving gases (probably H₂O and HF). The reaction was completed in several minutes to give an opaque solution. The solution should be left for several minutes to precipitate the black solid. Then the supernatant solution was decanted to the other arm (Tube B) and HF was condensed back to Tube B by cooling Tube A at -176°C. This procedure was repeated several times. In this procedure, large excess HF is preferably supplied since the vapor pressure of HF becomes very low due to the large solubility of AgF in HF at room temperature. A white solid (silver bifluoride, Ag(HF)₃F) was crystallized after evacuating HF. AgF was obtained by subsequent elimination of HF with heating Ag(HF)₃F to 70 – 80°C by a water bath.

AgF is light sensitive, some black particles being formed. Therefore, it was kept in darkness by wrapping the container with aluminum foil. The purification by decantation in anhydrous HF should be carried out just before use when very pure AgF was needed for the experiment.

A.2 Preparation of tungsten oxide tetrafluoride (WOF₄)

WOF₄ was prepared by the hydrolysis of tungsten hexafluoride (WF₆, Ozark-Mahoning) as described elsewhere[1]:

\[
WF_6 + H_2O \rightarrow WOF_4 + 2HF
\]  (2)

Since WOF₄ easily reacts with H₂O to form oxonium complex salts, H₃OWOF₃ and H₃OW₂O₂F₉, or tungsten bronze (blue solid), H₂O must be supplied very slowly to excess WF₆. It is a convenient way to supply H₂O formed by a sluggish reaction of silica (SiO₂) and HF:


\[
\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}
\]  

Quartz wool (Toshiba) was charged in an FEP tube. It must not be stuffed in the bottom of the reactor otherwise the HF whose specific gravity (0.987 g cm\(^{-3}\)) is lower than that of WF\(_6\) (3.44 g cm\(^{-3}\)) does not interact with it. HF and WF\(_6\) were condensed on it, the amount of the former being large enough to dissolve WOF\(_4\). The reaction was continued overnight. After evacuating excess WF\(_6\) and HF, the mixture of WOF\(_4\) and oxonium complex salts was obtained. Then WOF\(_4\) was separated from the mixture by sublimation at \(-50^\circ\text{C}\) under a reduced pressure. No impurity was detected by X-ray powder diffraction.

WOF\(_4\) was also obtained by fluorination of WO\(_3\) (Nakarai Tesque, purity 99.5%), which was more efficient to prepare a large amount of WOF\(_4\):

\[
\text{WO}_3 + 4\text{F}_2 \rightarrow \text{WOF}_4 + 2\text{OF}_2
\]  

WO\(_3\) powder was put in a Ni cup which was placed in a Monel reactor. F\(_2\) (2 atm) was introduced in the reactor at room temperature. The reactor was heated to 300\(^\circ\text{C}\) with the valve of the reactor closed in order to avoid the deposition of WOF\(_4\) in the vacuum line. The reaction was continued for several hours. The reactor was then cooled down to room temperature and the gases in it were evacuated. F\(_2\) (2 atm) was refilled again and allowed to react with WO\(_3\) for several hours at 300\(^\circ\text{C}\). This process was repeated several times. Finally, a white solid deposited on the cooled lid of the reactor was collected. The purity of WOF\(_4\) was confirmed by X-ray powder diffraction. Further purification was not necessary in this method.

**A.3 Preparation of uranyl fluoride (UO\(_2\)F\(_2\))**

UO\(_2\)F\(_2\) was prepared by fluorination of U\(_3\)O\(_8\) powder[3]:

\[
\text{U}_3\text{O}_8 + 5\text{F}_2 \rightarrow 3\text{UO}_2\text{F}_2 + 2\text{OF}_2
\]  

U\(_3\)O\(_8\) was prepared by oxidation of UO\(_2\) (Furukawa Denki Kogyo, depleted uranium) in a
porcelain crucible in air at -800°C. \( \text{U}_3\text{O}_8 \) was put in a Ni cup which was placed in a Monel reactor. \( \text{F}_2 \) (2 atm) was introduced in the reactor at room temperature. The temperature of the reactor was elevated to 200°C and held for several hours monitoring the pressure. After cooling the reactor down to room temperature and evacuating the gases in it, \( \text{F}_2 \) (2 atm) was introduced again and allowed to react with residual \( \text{U}_3\text{O}_8 \) at 200°C for several hours. This process was repeated several times. A pale yellow solid was remained in the Ni cup. Small amount of black material which was probably \( \text{U}_3\text{O}_8 \) was remained in the solid although the X-ray powder pattern of the solid detected only \( \text{UO}_2\text{F}_2 \). The reaction seems to be very slow. However, the temperature must not be elevated over 200°C because subsequent fluorination of \( \text{UO}_2\text{F}_2 \) to \( \text{UF}_6 \) occurs.

\( \text{UO}_2\text{F}_2 \) was also prepared by hydrolysis of \( \text{UF}_6 \)[4,5]:

\[
\text{UF}_6 + (2+n)\text{H}_2\text{O} \rightarrow \text{UO}_2\text{F}_2 \cdot n\text{H}_2\text{O} + 2\text{HF}
\]

Where \( n = -2 \). \( \text{UF}_6 \) was prepared by fluorinating \( \text{UO}_2 \) (Furukawa Denki Kogyo, depleted uranium) in a nickel metal reaction vessel at around 500°C, and distilled into a Monel metal container after evacuating volatile gases at 0°C for a while. \( \text{H}_2\text{O} \) was put in an FEP reactor and frozen at -176°C. After evacuating air above the ice, excess \( \text{UF}_6 \) was condensed on it. After the interaction for several hours, a viscous yellow solution was obtained. After evacuating excess \( \text{UF}_6 \) and volatile materials with warming the reactor, a yellow solid was formed. The solid was charged in a Pyrex glass reactor and dried under vacuum at 200°C for several hours. The temperature should not exceed 200°C since the decomposition of \( \text{UO}_2\text{F}_2 \) occurs[3]. The product was confirmed to be anhydrous \( \text{UO}_2\text{F}_2 \) by X-ray powder diffraction[6] and Raman spectroscopy[7].

A.4 Preparation of uranium pentafluoride (\( \text{UF}_5 \))

\( \text{UF}_5 \) (β-form) was prepared by the reaction of \( \text{UF}_6 \) and carbon monoxide (CO, Takachiho Kagaku Kogyo, spectroscopic grade) under irradiation of UV light:
UF₆ was condensed in a Pyrex glass bulb (1000 cm³) and CO (1 atm) was introduced in it. The bulb was irradiated by UV light of a mercury lump (Hitachi UM-102) for a day. A greenish solid was deposited on the wall of the bulb. After cooling the cold finger of the bulb at 0°C to trap unreacted UF₆, the gases in the bulb was evacuated and CO (1 atm) was introduced again. This step was repeated several times. The reaction is very slow and the deposition of UF₅ on the wall prevented UV light from irradiating the inside of the bulb. Therefore, it takes several days to prepare even a few grams of UF₅.

UF₅ is also prepared by proportionation of UF₆ and UF₄ in HF at room temperature[8]:

\[ UF_6 + UF_4 \rightarrow 2UF_5 \]  \hspace{1cm} (8)

and reduction of UF₆ by PF₃ in HF[9]:

\[ 2UF_6 + PF_3 \rightarrow 2UF_5 + PF_5 \]  \hspace{1cm} (9)

These methods were not tried in this study.

A.5 Preparation of bismuth pentafluoride (BiF₅)

BiF₅ was prepared by fluorination of bismuth metal:

\[ Bi + 5/2 F_2 \rightarrow BiF_5 \]  \hspace{1cm} (8)

Granular Bi (Nakarai Tesque, 99.5%) metal was put in a Ni cup which was placed in a Monel reactor. F₂ (1.5 atm) was introduced in the reactor at room temperature and interacted with Bi at 500°C for several hours with the valve of the reactor closed in order to raise the pressure of F₂ and avoid the deposition of BiF₅ in the vacuum line. The reaction was slow in this condition where Bi melted (m.p. 271.3°C[2]). A white solid was deposited on the lid of the reactor. The X-ray powder pattern of the solid detected some impurities. BiF₅ was purified by sublimation at 120°C under a reduced pressure. This preparation was not successful since unreacted Bi was always remained and difficult.
BiF₃ was also prepared by fluorination of Bi₂O₃ (Nakarai Tesque, purity 99.9%):

\[ \text{Bi}_2\text{O}_3 + 8\text{F}_2 \rightarrow 2\text{BiF}_3 + 3\text{OF}_2 \]  

(9)

Bi₂O₃ was put in a Ni cup which was placed in a Monel reactor. F₂ (~5 atm) at room temperature was transferred to the reactor by condensation. The reactor was heated at 500°C with the valve of the reactor closed in order to raise the pressure of F₂ and avoid deposition of BiF₃ in the vacuum line. The reaction was continued for several hours. A white solid deposited on the lid of the reactor was collected. X-ray powder diffraction of the solid detected no impurity.

BiF₃ is very reactive with water to form HF and ozone (O₃). Therefore, when the tools adhered with BiF₃ are washed with water, one should take much care. A brown solid (probably oxides or oxide fluorides of Bi) sticks to the tools when washed with water. It is easily removed by washing with dilute HCl solution.
References

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