Modern Synthesis Processes and Reactivity of Fluorinated Compounds

Progress in Fluorine Science Series

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Photochemical Syntheses of Fluorides in Liquid Anhydrous Hydrogen Fluoride

20

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Chapter Outline

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1. Introduction

For the preparation of fluorides with transition or main group elements in the highest oxidation states,[1] quite drastic conditions such as high temperature and high pressure of fluorine are usually required. At ambient or room temperature (RT) they can be synthesized in liquid anhydrous hydrogen fluoride (aHF) by the use of strong oxidizers such as KrF_2[2] or by rarely used approaches involving PtF_6[3]; in situ−generated solvated O_2F[4]; aHF solutions of cationic Ag(II), Ag(III), or Ni(IV)[5,6,7]; etc. ultraviolet (UV)-irradiated F_2 has been widely used in the past for the preparation of various fluorine compounds in the gas phase.[8,9] In 1998, a photochemical approach using UV-irradiated F_2 in liquid aHF at ambient temperature was reported for the first time.[10] The reader is referred to an extensive reviews about the various methods of syntheses of fluorides reported by Grannec and Lozano[11] and Lutar et al.[9]

In this chapter, I present in more detail the photochemical approach of syntheses of various transition metal fluorocompounds in the highest oxidation states at ambient temperature. Additionally, some examples of the syntheses of main group fluorides are given. The primary intention of this contribution is to summarize results of photochemical preparations of various fluorides in liquid aHF at ambient temperature using elemental fluorine as the fluorinating agent. For comparison, some reactions showing how far oxidation with elemental fluorine at ambient temperature and using neutral or basic aHF as a solvent will go without using UV source are also given. The expression neutral aHF means that there are no fluoride ion donors, such as AF (A = Li, Cs), present in the starting reaction mixture. On the contrary, the term basic aHF refers to reactions in which such sources take part in chemical reactions. The highest oxidation states are more likely to be achieved in anionic parts of ternary fluorides rather than in binary fluorides.[12] On the other side, since the electronegativity of a given oxidation state must be higher in a cation than in neutral or anionic relatives, it follows that low oxidation states are more likely to be achieved if oxidations with F_2 are carried out in aHF solutions made acidic[13] with fluoride ion acceptors as Lewis fluoroacids (e.g., AsF_5, SbF_5).

The requirements of photochemical syntheses with elemental fluorine in aHF and the reaction mechanism are described in Sections 2 and 3. In Section 4, examples of F_2 fluorination in neutral and basic aHF with or without the presence of UV light, which I managed to collect from the available literature, are listed.

2. Requirements of Photochemical Syntheses With Elemental F_2 in Anhydrous HF

2.1 Caution

aHF, elemental fluorine, and some fluorides are highly reactive, toxic, and corrosive. Therefore working with them is demanding and potentially dangerous. They must be handled using appropriate apparatus and protective gear, and experiments should be performed in well-ventilated hoods. The exposure to UV sources should also be avoided because of possible damage to the skin and specially the eyes. One should never look directly at an unshielded operating lamp unless protecting glasses are worn. UV lamps can generate unsafe amounts of ozone. Before starting for the first time any photochemical experiment, it is recommended to consult a member of an experienced fluorine group.

2.2 Reaction Vessels and Ultraviolet Lamps

Since aHF etches glass and some reactions require the use of higher pressures of elemental fluorine (up to 6 bars), translucent fluorocarbon plastics are the only choice of materials for reaction vessels. Two such most common materials are FEP (hexafluoropropylene-tetrafluoroethylene copolymer) and PFA (tetrafluoroethylene-perfluoroether copolymer). Although, their chemical compositions are slightly different, their mechanical and chemical properties, for example, chemical inertness against aHF and remarkable kinetic stability to elemental fluorine and other strong oxidizers, are practically the same. Both materials are transparent to visible and near-UV light. The visible transparency is important because it is possible to visually follow what is happening during the reaction and the UV transparency because it provides effective photodissociation of elemental fluorine inside the reaction vessel by a UV source that is outside it. Reaction vessels are equipped with valves. Their bodies and needles are made from polytetrafluoroethylene (PTFE), which are fitted with metal collars with appropriately located metal treads. In Fig. 20.1 there is a typical reaction vessel equipped with valve (modified version of that shown in Ref. 14 used in our laboratory). Before using, they should be checked for the pressure that they could sustain. In some of our reactions, pressures of elemental fluorine and aHF inside reaction vessels at RT reach up to 6 bars.

Photochemical reactions can be performed using sunlight, although this is not a very common approach because of the variability of this source (intensity changes with time, its spectrum varies because of the impurities in atmosphere, etc.).[15] By far the most useful and widely used UV light sources are the mercury arc lamps made of two metal electrodes encased in glass or silica bulb and filled with mercury.[15,16] There are three basis types, i.e., low-, medium-, and high-pressure Hg arc

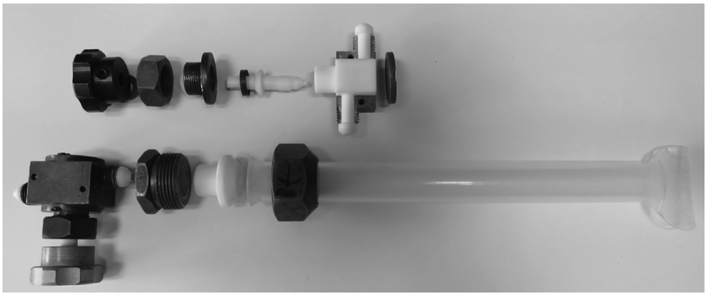

Figure 20.1 Disassembled FEP/PFA reaction vessel equipped with polytetrafluoroethylene valve used for reactions in liquid anhydrous HF.

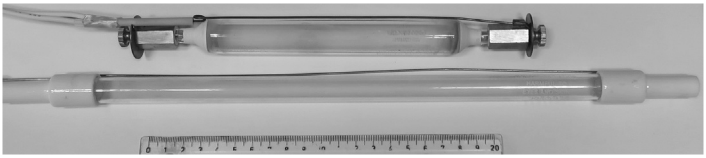

Figure 20.2 Two different models of medium-pressure Hg arc lamps (450 W, Ace Glass, USA).

lamps (Fig. 20.2). The low-pressure arc lamp gives practically a single line at 253.7 nm. The most useful ones are medium- and high-pressure Hg arc lamps, which emit many lines in the UV and visible regions (Fig. 20.3).

All Hg arc lamps have to be used with a proper power supply, and they should not be connected directly to the electricity grid. During their operation, Hg arc lamp

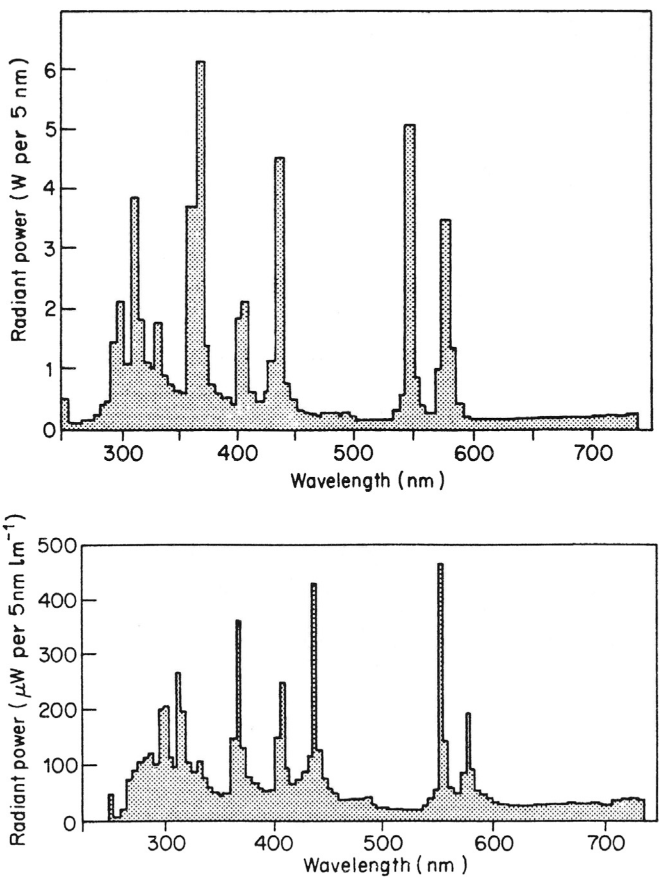

Figure 20.3 Emission spectra of medium-pressure (top) and high-pressure (bottom) Hg arc lamps.
Suppan, P. 1994. Chemistry and Light, The Royal Society of Chemistry, Cambridge - Reproduced by permission of The Royal Society of Chemistry; http://dx.doi.org/10.1039/9781847550439-00216.

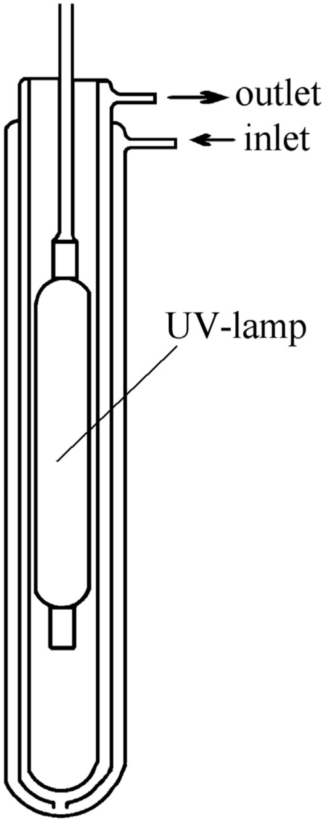

Figure 20.4 Tap-water-cooled immersion well.

surfaces get extremely hot and therefore they should be cooled down. The satisfactory cooling system for the lamp housing is shown in Fig. 20.4. The water-cooled immersion well is made of glass and cooled with tap water.

2.3 How to Perform Synthesis

In a typical reaction, solid starting materials are loaded into a reaction vessel in a dry box. aHF (4−8 mL) is condensed onto the solid at 77 K. With its long liquid range (melting point, −83.55°C; boiling point, 19.51°C), wide electrochemical window (useable potential range of about 4.5 V between anodic and cathodic generation of F_2 and H_2), excellent ionizing solvent (dielectric constant 83.6 at 0°C and 175 at −73°C), the widest range of acidity−basicity of any of superacids, and remarkably robust nature both oxidatively and reductively, the use of superacid aHF seems to be the best choice.[17,18] In referring to aHF we must have in mind the convention used by most chemists, certainly by fluorine chemists. Aqueous solutions of hydrogen fluoride are referred to as "hydrofluoric acid," whereas the term "anhydrous hydrogen fluoride (aHF)" refers to the pure compound.

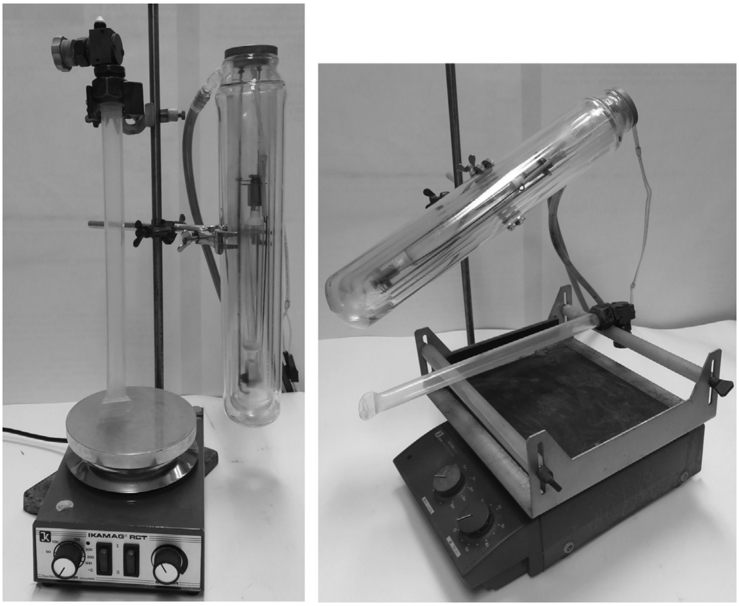

Figure 20.5 Experimental setup for photochemical syntheses using magnetic stirrer (left) or mechanical orbital shaker (right).

Concerning addition of fluorine, there are two possibilities. In the first, the reaction mixture is brought to ambient temperature and fluorine is slowly added to a preferred pressure. In the second method, fluorine is condensed onto frozen aHF/reactants mixture at 77 K from the known volume with known pressure. In both cases, it is better to start with lower pressure of fluorine and later increase it by step-by-step additions.

After the reaction vessel is filled with all reactants, it is placed near tap-water-cooled UV source. The lamp assembly should be operated in a hood or well-ventilated area, which is additionally protected against exposure to UV light. The reaction mixture should be well mixed by a magnetic stirrer (when PTFE-coated stirring bar is added inside the reaction vessel) or by mechanical orbital shaker on which the reaction vessel is mounted in horizontal position (Fig. 20.5). In the cases of prolonged reaction times (more than few days), the second method is more preferable, specially if the products are only sparingly soluble or insoluble in aHF. When PTFE-coated stirring bars were used in such cases, their abrasion was observed, i.e., their shape changed to egglike shape. Additionally, when the products were hydrolyzed in distilled water for chemical analysis, small PTFE particles were observed floating in the solutions.

3. Reaction Mechanism

The first thing that has to be stressed is that in the case of UV-photodissociated F_2 reactions, UV light is not a catalyst.[15] In photochemical reactions, UV light (and light generally) acts as a reactant because in those reactions light is absorbed and its energy is used to split F_2 molecule. It does not come out again, and it cannot be used after the reaction. The most important industrial process (at least in terms of quantity of produced chemicals) is photochemical chlorination of polymers.[15] By utilizing the UV energy by various approaches, the Cl_2 molecules are homolytically dissociated into Cl• atoms, which are in fact free radicals. They react with hydrocarbons through substitution and insertion processes. Photochemical reactions between UV-irradiated F_2 molecules and various inorganic starting materials in liquid aHF as a solvent have a similar beginning, i.e., photodisscosciation of diatomic molecules, but then the similarity ends. They are not chain reactions in which new F• radicals are formed as in the case of reactions of UV-irradiated Cl_2 with hydrocarbons. The explanation of light-promoted F_2 reactions was given in the first article about the use of photochemical reactions with elementary F_2 in liquid aHF.[10] The light absorption maximum of F_2 molecule is close to 300 nm with a broad tail into the visible part. This absorption is associated with the promotion of the electron from bonding to nonbonding molecular orbital. The consequence is dissociation of F_2 molecule to F• atoms (i.e., radicals). The important thing is the length of their effective lifetime. If F• radicals would recombine with each other very quickly, then there would be no time to react with reactants in aHF, and therefore photochemical reactions would make no sense. It was proposed that in the strongly basic aHF, the effective lifetime of F• atom is prolonged by the formation of species such as $F_2^{\bullet-}$ or its hydrogen-bonded solvates such as $[F_2^{\bullet}HF]^-$ or $[F_2^{\bullet}2HF]^-$.[10] Because of charge repulsion is less likely that such species quickly regenerate F^2 as in the case of uncharged $F^{\bullet}$. On the basis of comparison of electron affinities of $F_{(g)}^{\bullet}$ (3.399 eV) and $F_{2(g)}$ (3.10 eV), the $F_2^{\bullet-}$ must be less bound than the $F_{2(g)}$, i.e., $F_2^{\bullet-}$ or its HF solvates are better fluorine atom sources than F_2 itself. Additionally, charged $F_2^{\bullet-}$, $[F_2^{\bullet}HF]^-$, and $[F_2^{\bullet}2HF]^-$ species are also nucleophilic. This mechanism has been given for basic aHF in which well-soluble fluoride-ion donors (e.g., alkali metal fluorides) are present in the solutions increasing the concentrations of solvated F^- species. The extent of self dissociation of pure aHF is very small ($K_{ap} \sim 10^{-11}$).[17] When binary fluorides are synthesized in neutral aHF, there are no additional F^- donors in the form of alkali metal fluorides present in the reaction mixture. The concentrations of $F_2^{\bullet-}$, $[F_2^{\bullet}HF]^-$, and $[F_2^{\bullet}2HF]^-$ species must be much lower. However, the reactions proceed anyway, although in general, much longer times are requested than for the syntheses of ternary fluorides. The low or nonsolubility of starting binary fluorides and final products is also slowing down the reactions. The reactions are of course much faster when products are removed from the surface of the reactants by dissolving in aHF.

4. Examples of F_2 Fluorinations in Liquid Anhydrous HF at Ambient Temperature

The goal of this chapter is to summarize the photochemical syntheses of fluorides since the first published report in 1998.[10] For some elements how far oxidation with elemental fluorine at ambient temperature and in aHF as a solvent goes without using

UV source is also summarized. Many examples from our laboratory, which have not been published before, are reported. The given examples are limited mostly to reactions with elemental F_2, proceeding in aHF at ambient temperature (RT) with or without the use of UV light. Therefore, the syntheses of various binary and ternary fluorides using other strong oxidizers as KrF_2, KrF^+, and PtF_6 are not treated in this chapter. Similarly, with a few exceptions, the reactions that proceed with HF, F_2, or HF/F_2 mixtures at elevated temperatures are not included. The photochemical syntheses that take place in the presence of UV source at low or ambient temperatures without the presence of liquid aHF are also not part of this contribution (e.g., synthesis of XeF_2, KrF_2, O_2F_2, SF_6, ClF_5, NF_4^+ salts).

4.1 Fluorides of the Transition Metal Elements

4.1.1 Titanium, Zirconium, and Hafnium

The highest oxidation state +4 in MF_4 (M = Ti, Zr, Hf) tetrafluorides can be quite easily achieved, and their syntheses are well described in many general books of inorganic chemistry. Herein, I would like just to mention that the reaction between $TiCl_3$ and aHF at RT produces TiF_3, which can be further fluorinated with elemental F_2 in aHF at RT yielding pure TiF_4.[19]

In the available literature, I have not been able to find any data about fluorination of those metals or their compounds in lower oxidation states with F_2 in aHF at RT. There is only a report that Ti, Zr, and Hf react with gaseous aHF at 200−225°C yielding TiF_3, ZrF_4, and HfF_4, respectively.[20]

4.1.2 Vanadium, Niobium, and Tantalum

With V, Nb, and Ta the situation is very similar as in the case of Ti, Zr, and Hf with the main difference being that the highest oxidation state for V, Nb, and Ta is +5. The reports about preparation of V, Nb, and Ta compounds in 5+ oxidation state at RT with F_2 and aHF are scarce.

My attempt to prepare VF_5 at RT by reaction between VF_3 and F_2 in aHF resulted in impure VF_5 contaminated with VOF_3. Niobium powder reacts with gaseous aHF at 250°C and tantalum below 200°C.[21,20] For Nb, the volatile product is NbF_5 and the residue nonattacked metal, whereas for Ta, the product is nonattacked metal, TaF_5, and probably TaF_3.

There are no data regarding what happens if fluorine is added onto metal/liquid aHF mixtures, but the preparation of $LiMF_6$ (M = Nb, Ta) from the elements and LiF in aHF by F_2[22] shows that Nb and Ta can be easily oxidized at RT to their highest oxidation state +5 using F_2 in aHF made basic with alkali fluorides with no need for UV light.

4.1.3 Chromium, Molybdenum, and Tungsten

Attempts to fluorinate Cr powder (100 mesh) with ClF_3 in the presence of F_2 (2 bar) in aHF solution at RT for 16 h were unsuccessful.[23] This inertness should be of kinetic origin, wherein in liquid aHF, insoluble CrF_3 formed on the surface of metal can block further reaction. My attempt to prepare CrF_4 by F_2 fluorination of CrF_3 in aHF at RT was also unsuccessful.

The $ACrF_6$ (A = Li−Cs) compounds containing Cr(V) can be prepared by photochemical reactions with elemental F_2 on AF/CrF_3 mixtures in liquid aHF at RT. In the presence of UV source, all Cr^{3+} is oxidized by fluorine to Cr^{5+} yielding deep red clear solutions from which pure $ACrF_6$ compounds are isolated.[24] The K, Rb, and Cs salts could be recovered at RT by pumping away the excess fluorine and aHF solvent. When $NaCrF_6$ had been isolated at the same conditions, release of CrF_5/F_2 was observed, resulting in $NaCrF_6$/Na_2CrF_6. This could be avoided with the isolation at temperatures below 243 K. Dry $NaCrF_6$ is stable at RT and could be stored in a dry box. $LiCrF_6$ could be isolated in the same manner, but in contrast to $NaCrF_6$ it immediately starts to decompose at RT. All $[CrF_6]^-$ salts are deep red, moisture-sensitive crystalline solids. Single crystals of $ACrF_6$ (A = Na, K, Rb, Cs) were obtained upon crystallization from corresponding solutions, and their crystal structures were determined. $KCrF_6$, $RbCrF_6$, and $CsCrF_6$ crystallize in well-known $KOsF_6$ type structure, whereas $NaCrF_6$ exhibits polymorphism. The trigonal phase of $NaCrF_6$ is analogous to the well-known $LiSbF_6$ structure, whereas the crystal structure of orthorhombic modification appears to be a previously unknown structure.

As a fluorinating agent, ClF has been placed below elemental F_2 in reactivity. Since reactions of ClF with elemental tungsten and molybdenum proceed smoothly at ambient temperature,[25] it could be assumed that their fluorination with F_2 in liquid aHF at RT will also give WF_6 or MoF_6 in the highest known oxidation state +6.

4.1.4 Manganese and Rhenium

Elemental fluorine oxidizes MnF_2 in liquid aHF as a solvent at RT yielding pure MnF_3.[26] In the presence of UV source, MnF_2 is completely oxidized by photodissociated F_2 in aHF to MnF_4.[27] The MnF_4 obtained was poorly crystallized and, therefore it was not possible perform X-ray powder diffraction analysis. In its Raman spectrum, a vibrational band at 1834 cm^{-1} typical for the O_2^+ cation was observed showing that an O_2^+ salt was present in the final product. However, the O_2^+ cation is a very good Raman scatterer and its mass amount could be less than 1%. The presence of oxygen can be attributed to impure MnF_2 or to slow diffusion of O_2 or H_2O through the wall of FEP/PFA reaction vessel.

Elemental fluorine is also capable of oxidizing Mn^{II} to Mn^{IV} in aHF made basic with AF (A = alkali metal) at RT in aHF in the absence of UV source. The effectiveness of the oxidation for the same period of time depends on the basicity of aHF (starting amount of alkali metal fluoride). However, in the absence of a UV source, these reactions are incomplete and give mixtures of products, e.g., $AF\cdot nHF$, $AMnF_4$, A_2MnF_6, and MnF_3. Pure A_2MnF_6 (A = Li, K, Rb, Cs) phases can be obtained only by photochemical reactions.[27] An attempt to prepare $CsMn^VF_6$ by oxidation of MnF_2 with UV-irradiated F_2 in the presence of equimolar amount of CsF in aHF failed. The final product of this reaction was a mixture of MnF_4 and Cs_2MnF_6. Similarly, my attempt to prepare $CsMnF_6$ using KrF_2 instead of photodissociated F_2 in liquid aHF at RT was also unsuccessful.

I tried the reaction between rhenium metal (powder, 210 mg) and elemental F_2 (6 bar) in liquid aHF (6 mL) at RT. Since there was no visible reaction, the reaction vessel was exposed to UV light. After a few days, Re metal dissolved and transparent solution was obtained. The remaining F_2 was pumped away at 77 K. Raman spectrum of the solution and IR spectrum of the gaseous product corresponded to literature data of ReF_6. The solution was cooled down to −70°C, and volatiles were pumped away. First there was yellow solid visible in liquid aHF, but after 8 h of pumping, nothing was left in the reaction vessel. According to this result, only yellow ReF_6 has been formed with no indication of known ReF_7. The reactions with addition of CsF (molar ratio CsF:Re = 1:1); with or without the presence of UV light proceeded in the same manner, yielding only a mixture of ReF_6 and $CsF \cdot nHF$.

4.1.5 Iron, Ruthenium, and Osmium

The fluorination of FeF_2 by elemental F_2 in liquid aHF at RT readily proceeds to FeF_3. All my attempts to prepare $Cs_2Fe^{IV}F_6$ by reaction between 2CsF, FeF_3, and UV-irradiated F_2 (8 bar in 35 mL FEP reaction vessel) in liquid aHF (8 mL) at RT or by reaction between 2CsF (0.5 mmol), FeF_3, (0.25 mmol) and KrF_2 (0.5 g) in liquid aHF (4 mL) at RT failed. Similarly, the attempt to synthesize $CsFe^{V}F_6$ by reaction of CsF (0.45 mmol) with FeF_3 (0.45 mmol) and KrF_2 (0.3 g) in aHF was also unsuccessful. In all cases, FeF_3 and $CsF \cdot nHF$ were recovered.

In 1996, two articles from two different groups working on fluorine were published, both reporting about the room temperature oxidative fluorination of platinum metals and gold by elemental fluorine in aHF.[28,29] After reaction between ammonium fluoride (NH_4F), Ru metal, and fluorine gas in aHF at RT, a cream-colored insoluble precipitate and a small quantity of unreacted metal powder were obtained. On drying, the precipitate turned sandy brown. According to IR data, the obtained product was Ru(V) compound $(NH_4)RuF_6$, which was readily reduced by moisture to $(NH_4)_2(RuF_6)$.[29] The F_2 with aHF made basic with KF dissolves Ru metal to give Ru(V) compound $KRuF_6$; however, when LiF is substituted for KF, the oxidation is slower and the ultimate product is Ru(IV) compound Li_2RuF_6. This difference is attributed to the low solubility of Li_2RuF_6 and the high solubility of K_2RuF_6 in the aHF solvent.[28]

Reaction between NH_4F, Os metal, and elemental F_2 in aHF at RT produced a yellow-green solution and some unreacted metal powder from which a white powder contaminated with the blue-gray metal was recovered after removal of the solvent. The IR spectrum could be assignable to Os(V) compound $(NH_4)OsF_6$.[29] When LiF was used instead of NH_4F, the $LiOsF_6$ with Os(V) was obtained.[28] It is unusual and unexplained why in the reaction done in the same manner, but using KF instead of LiF, there was no detectable formation of either K_2OsF_6 or $KOsF_6$.[28]

For Ru and Os metals, there are no reports regarding what happens when they, or their binary or ternary fluorides in oxidation state +5 (or lower), are treated with UV-irradiated elemental fluorine in neutral or basic liquid aHF. Otherwise, the highest oxidation state achieved in corresponding fluorides is +6 (RuF_6 and OsF_6).[1] Neither

Ru nor Os hexafluoride reacts with alkali metal fluorides, although NO[OsF_7] was reported to be formed along with NO[OsF_6] from NOF and OsF_6.[30]

4.1.6 Cobalt, Rhodium, and Iridium

Reaction between pink CoF_2 with excess of elemental fluorine (approximately 1.5−4) in liquid aHF at RT proceeds smoothly, and the course of reaction could be followed by the change in colors of the solids (starting compound and product are virtually insoluble in aHF), and by the consumption of fluorine followed by the drop in its pressure. The obtained product is pure light brown CoF_3.[26] No attempts have been made to prepare ternary Co(IV) compounds (e.g., Cs_2CoF_6) using photodissociated F_2, since it is known that $[CoF_6]^{2-}$ is unstable in liquid aHF at RT and it decomposes above 10°C with the formation of F_2 and some mixed Co(III)/Co(IV) solid product.[31] The rate of decomposition can be slowed by a factor of four by the addition of excess CsF to the solution.

When Rh metal was treated with elemental F_2 in the presence of NH_4F or LiF at RT in liquid aHF there was no indication of any complex rhodium fluoride having been formed. When the solvent was removed, only unreacted Rh metal and NH_4F or LiF, respectively, were recovered.[28,29] On the contrary, when a better fluoride ion donor such as CsF was used in our laboratory, $CsRhF_6$ was quantitatively obtained.

When I tried the reaction between Rh metal with UV-photolyzed F_2 in aHF at RT, the liquid phase turned yellow or sometimes yellow-brown. The large amount of insoluble dark residue was of different color than the starting Rh. After a few days, the reaction vessel was cooled down to −15°C and volatiles were pumped away for 3 days through the trap cooled in liquid nitrogen, wherein no coloration was observed. Finally, the sample was warmed to RT and pumped further. A small amount of yellow-red frozen solid was observed in the cold trap. Raman spectrum and X-ray powder diffraction analysis of the recovered dark red product (in which larger metallic pieces were still visible) were in agreement with the presence of starting Rh and RhF_5, whereas the Raman spectrum of the yellow-red compound caught in the trap corresponded to a mixture a RhF_5 and O_2RhF_6. The presence of the latter could be explained by the possible formation of RhF_6, which is able to oxidize traces of O_2 forming O_2RhF_6. It is evident that oxidation of Rh metal under the described conditions goes to Rh(V)/Rh(VI). However, direct fluorination of Rh metal with UV-irradiated F_2 in liquid aHF at RT is not a very suitable method for the preparation of pure RhF_5 or even less for the synthesis of RhF_6.

Fluorination of Ir metal by F_2 in the presence of NH_4F in liquid aHF at RT resulted in a gray, highly moisture-sensitive HF-insoluble precipitate.[29] Beside the characteristic vibrational bands for the $[NH_4]^+$ cations, an additional vibrational band at 633 cm^{-1} assignable to $[IrF_6]^-$ was observed in the IR spectrum of the isolated product showing that the latter is an Ir(V) compound NH_4IrF_6. Reactions of LiF or KF with Ir metal oxidized by elemental F_2 in liquid aHF at RT yield sparingly soluble yellow $LiIrF_6$ and $KIrF_6$, which could be crystallized from yellow (Li) and roseate (K) solutions.[28,32]

Similarly, as in the case of Ru and Os, there are no reports about reactions of Rh and Ir metals (or pentafluorides) by UV-irradiated F_2 in aHF to prepare binary or ternary

Rh(VI) and Ir(VI) fluorides. The highest known oxidation state achieved in corresponding binary fluorides is +6 (RhF_6 and IrF_6).[1] Neither of these react with alkali metal fluorides.

4.1.7 Nickel, Palladium, and Platinum

The report in 1998, about NiF_2 oxidizing at around 20°C to $[NiF_6]^{2-}$ by sunlight or UV-irradiated F_2 in liquid aHF containing dissolved alkali metal fluorides (LiF, NaF, KF, CsF), was the first one connected with the main topic of this chapter, i.e., photochemical syntheses of fluorides in liquid aHF at RT using elemental F_2.[10] The conversion to $[NiF_6]^{2-}$ was most effective with a saturated solution of KF in aHF and a large excess of alkali metal fluoride over NiF_2. With increasing concentrations of alkali metal solutions, fluorination becomes quicker and more efficient. This way, a dark purple-red Li_2NiF_6 was prepared for the first time. When syntheses were carried in sunlight, the particles of the aHF-insoluble pale yellow-green NiF_2 became black, before any coloring of the aHF solution occurred. This suggests that NiF_2 is first fluorinated to NiF_{2+x} ($x \leq 1$). This is the same phenomenon that I observed when NiF_2/F_2 reaction mixture in aHF was irradiated by UV light. However, the X-ray powder diffraction pattern of the isolated product corresponded to NiF_2 only. My attempt to prepare $CsNiF_5$ from stoichiometric amounts of CsF and NiF_2 by photochemical reaction, as described for Cs_2NiF_6, failed. The obtained solid was a mixture of Cs_2NiF_6 and $CsF \cdot nHF$.

Reaction between Pd powder (black or gray) in liquid aHF with excess of elemental fluorine proceeds smoothly at RT, and the course of reaction is followed by the consumption of fluorine, which is followed by the drop in its pressure. The product obtained is black, mixed oxidation state Pd_2F_6 ($Pd^{II}Pd^{IV}F_6$).[26] Even when PdO (1.6 mmol) and F_2 (13 mmol) in aHF were left to react for a longer time, the reaction was not completed. Only about 60 mol% of starting PdO was converted into Pd_2F_6 after 48 days.[33]

When I treated Pd metal/F_2 reaction mixture in liquid aHF with UV light, black Pd_2F_6, which was formed first, started to change its color to brick-red, whereas the liquid aHF stayed colorless. Raman spectrum of in aHF-insoluble solid showed, beside vibrational bands, which could be assigned to PdF_4, the presence of O_2^+ salt. After fluorine was pumped away, small amount of Lewis acid AsF_5 was condensed the inside reaction vessel. The liquid phase was separated from the insoluble one. The product recovered from decanted solution was colorless O_2AsF_6, and the insoluble residue was brick-red PdF_4.

In aHF made basic with AF (A = Li, K, Cs or $[NH_4]^+$), the fluorination of Pd metal with elemental F_2 in aHF at RT resulted in the formation of yellow-orange solutions from which yellow A_2PdF_6 and orange $(NH_4)_2PdF_6$ compounds were isolated.[28,29] The obtained Li_2PdF_6 is only slightly soluble in aHF and it is isostructural with tetragonal Li_2PtF_6. X-ray powder diffraction analysis of K_2PdF_6 showed the presence of both the known trigonal (K_2GeF_6-type structure) and hexagonal phases (K_2MnF_6-structure type), whereas that of Cs_2PdF_6 corresponded to cubic phase (K_2PtCl_6-type structure).

In the case of the product prepared by the reaction between Pd and excess of CsF in the presence of fluorine in aHF, it was noticed that the isolated solid turned from yellow to brown and finally to black, although the sample was kept all the time in the dry box.[34] In the Raman spectrum, besides vibrational bands of PdF_6^{2-} anion (561, 546, and 235 cm^{-1}), two additional bands at 410 and 510 cm^{-1} appeared. With time, their intensity increased and the intensity of the bands belonging to the PdF_6^{2-} anion decreased. Such change in color was also observed for $(NH_4)_2PdF_6$, wherein the isolated product turned from yellow to brown overnight in the dry box.[29] The most likely cause of the color change of the isolated Cs_2PdF_6 is the presence of $CsF \cdot nHF$. Reactions between CsF and aHF yield $CsF \cdot nHF$ phases where n depends on the vacuum conditions and the temperature. When there is a mixture of Cs_2PdF_6 and $CsF \cdot nHF$, the latter slowly releases aHF causing the decomposition of the former, similar to the case of yellow solid $La_2(PdF_6)_3$ (prepared by mixing of aHF solutions of $La(AsF_6)_3$ and Cs_2PdF_6 in molar ratio 2:3) solvolysis when it is exposed to liquid aHF.[34] When Cs_2PdF_6 was prepared from reactants in molar ratio CsF:Pd = 2:1 or by deficit of CsF, there was no sign of decomposition even after weeks. The color of the bright yellow solid did not change, and the Raman spectrum did not show any additional bands except those belonging to the PdF_6^{2-} anion.

The attempted fluorination by elemental F_2 (with UV irradiation) of K_2PdF_6 and Cs_2PdF_6 in aHF at RT to prepare Pd(V) compounds were unsuccessful. The constant product weights and the negligible fluorine consumption indicated that there was no oxidation.[35]

Platinum metal was fluorinated by elemental F_2 in liquid aHF made basic with NH_4F at RT to give lemon-yellow solution from which air-stable yellow crystalline $(NH_4)_2PtF_6$ containing Pt(IV) was isolated on removal of all volatiles in vacuum.[29] The obtained formulation was supported by ^{19}F nuclear magnetic resonance and IR spectroscopy. The reaction with LiF instead of NH_4F gives very soluble light yellow tetragonal form of Li_2PtF_6.[28,29] The X-ray powder diffraction analysis of K_2PtF_6 prepared in the same manner showed only the trigonal form (K_2GeF_6-type structure).

Li_2PtF_6 has low solubility in aHF. When it is partly dissolved at ~20°C in liquid aHF, it yields a faintly yellow solution. After fluorine is added and the reaction mixture is placed (with agitation) in sunlight, the color of solution gradually intensifies, yielding bright yellow solution. The latter is decanted, and after all volatiles are removed, the Pt(V) compound $LiPtF_6$ is obtained ($LiSbF_6$-type structure). The residue is unreacted Li_2PtF_6. Although the remaining valence electrons of $[PtF_6]^{2-}$ constitute a weakly antibonding set of t_{2g}^6 symmetry, which has highly favorable exchange energy, the F atoms (radicals from sunlight irradiated F_2) in aHF solution break this configuration and generate $[PtF_6]^-$.[35] Analogous reaction with $[PdF_6]^{2-}$ does not occur since the tighter binding of 4d electrons relative to 5d electrons causes Pd(V) to be inaccessible, at least by using UV-irradiated F_2.[35]

Only MF_6 (M = W, Mo and Re) seem to be able to increase their coordination numbers by adding F^-. It seems that higher members of transition metal hexafluorides (M = Ru, Rh, Os, Ir, Pt) do not undergo expansion of their coordination sphere[36] forming AMF_7 or A_2MF_8 (A = alkali metal) compounds.

4.1.8 Copper, Silver, and Gold

The triply charged $[CuF_6]^{3-}$ anion with Cu(III) undergoes solvolysis in aHF. CuF_3 is formed from K_3CuF_6 as a red solid at −78°C, and it loses F_2 at −40°C.[37] Since the

$[MF_6]^{2-}$ anions contain one negative charge less than the $[MF_6]^{3-}$ ones, they are less basic and consequently less likely to solvolyze in superacid aHF. However, even at low temperature, the Cu(IV) compound Cs_2CuF_6 reacts with aHF to form dark brown solid.[38] At ambient temperature the decomposition is completed and the evolution of F_2 occur. Because of this, it is not expected that oxidation of Cu(II) by UV-irradiated F_2 in liquid aHF at RT will result in Cu(III) or Cu(IV) compounds.

AgF_2 was reported to be prepared by passing fluorine diluted with nitrogen through a solution of AgF in aHF.[39] Much more conveniently, AgF_2 is synthesized by fluorination of $AgNO_3$ with F_2 in aHF at RT with occasional removal of volatiles and reintroduction of F_2. With this method, used in our laboratory, fine powdered AgF_2 can be prepared. Such AgF_2 is very reactive toward many organic and inorganic compounds.[40,41]

Neither AgF nor AgF_2 gave $KAgF_4$ when treated with F_2 in solution of KF in liquid HF at $\sim 20°C$.[28] When yellow Ag(I) compound $AgAuF_4$ with very low solubility in liquid aHF was pressurized with F_2 and left in the sunlight without agitation for two days, it became dark green. After the solution was decanted, away the X-ray powder diffraction pattern of the residue showed the patterns of starting Ag(I) compound $AgAuF_4$ and newly formed Ag(II) compound $AgFAuF_4$.[42] In this experiment it had been anticipated that some $AgFAuF_6$ with Au(V) would form. But, even in the strong sunlight, the F_2 concentration in the described experiment must have vastly exceeded that of F atoms. The Ag^+ cation is effectively attacked by the highly electrophilic F_2 species, which will not oxidize $[AuF_4]^-$, the F• radicals are required for that.

AgF_2 dissolves at $\sim 20°C$ in aHF containing large excess of KF (~ 20 times more than the stoichiometric amount), with sunlight or UV-irradiated F_2 yielding bright yellow solution. Nearly quantitative conversion to Ag(III) compound $KAgF_4$ can be achieved with such concentrated KF solutions.[43] KHF_2 impurity can be removed as KPF_6 with PF_5 at 0°C. Preparation of $LiAgF_4$ is less efficient. My attempts to prepare pure $NaAgF_4$ and $CsAgF_4$ by reaction between AF (A = Na, Cs) and AgF_2 (molar ratio AF:AgF_2 = 1:1) resulted in $AAgF_4$ samples contaminated with Ag_3F_8 (i.e., mixed oxidation state fluoride $Ag(AgF_4)_2$).

Reactions between metallic Au and elemental F_2 in aHF at RT provide yellow Au(III) compounds, i.e., $AAuF_4$ (A = Li, K) salts.[28] Even prolongated fluorination failed to generate $[AuF_6]^-$ salts in liquid aHF at RT and fluorine pressures below 1 atm. When solutions of $[AuF_4]^-$ salts are further oxidized by photodissociated F_2 (using sunlight or UV light), the Au(V) compounds $AAuF_6$ (A = Li, K) are formed.[35] A similar reaction, which I tried between CsF, Au, and UV-irradiated F_2 in aHF at RT, gives light yellow $CsAuF_6$, sparingly soluble in aHF. O_2AuF_6 was also synthesized unintentionally in an attempt to prepare AuF_5 from AuF_3 and F_2 contaminated by O_2 in aHF employing photodissociation of F_2 by 20-day exposure to sunlight.[35] Otherwise, canary yellow O_2AuF_6 can be easily produced by treating of AuF_3 with O_2/F_2 in liquid aHF at RT in the presence of a UV source as done in our laboratory.

Beside M^IAuF_6 many $M^{II}(AuF_6)_2$ (M = Ni, Cu, Ag, Zn, Cd, Hg, Mg, Ca, Sr, Ba) compounds can be prepared from corresponding MF_2, AuF_3 and UV-photodissociated F_2 in liquid aHF at RT.[44] The only condition is that metallic cations in MF_2 are resistant to oxidation. In some cases the isolated products were contaminated with traces of

O_2AuF_6 due to the impure MF_2 or slow diffusion of O_2 through the wall of FEP/PFA reaction vessel. Mg, Ca, Sr, Ba, and Cd hexafluoridoaurates(V) are well soluble in aHF yielding yellow solutions. The Ni, Cu, and Zn salts are sparingly soluble, whereas the Hg and Ag salts are almost insoluble in aHF. Except $Ag(AuF_6)_2$, which is green, all other $M(AuF_6)_2$ compounds are yellow (from canary to dark yellow). Raman spectra and X-ray powder diffraction data indicate that Ni, Cu, Zn, and Mg salts are structurally related. Crystal structures of $Cd(AuF_6)_2$ and $Hg(AuF_6)_2$ were determined on single crystals.[45,46] Single crystals of $Mg(HF)AuF_4AuF_6$ were grown during the attempt to grow single crystals of $Mg(AuF_6)_2$.[45] $Mg(HF)AuF_4AuF_6$ is the only example of a mixed oxidation state Au(III)/Au(V) compound. An attempt to grow single crystal of $Ag(AuF_6)_2$ resulted in $AgFAuF_6$ instead.[46]

4.1.9 Zinc, Cadmium, and Mercury

It was reported that Zn and Cd react with gaseous aHF at elevated temperatures (160−220°C) yielding the corresponding difluorides.[20] Since there are many other much more convenient methods for their synthesis (e.g., preparations from carbonates, chlorides), their preparation by fluorination of the corresponding metals in liquid aHF is not the best choice. Additionally, reactions could be hindered by the passivation of metal surfaces by forming difluorides, which are only sparingly soluble in aHF.

4.1.10 Scandium, Yttrium, Lanthanum to Lutetium

Metallic Eu, Yb, and Sm react with aHF and dissolve with the evolution of H_2 and producing colorless (Eu, Yb) or yellow-orange (Sm) solutions containing the corresponding solvated Ln(II) cations and solvated fluoride anions.[47] Lanthanum and thulium metals showed slow reaction with aHF, but no evidence could be found for Ln(II) in solution. The respective LnF_3 and hydrogen were the only products observed. There was also a report about reactions of gaseous aHF with Sc, Y, La, Ce, Pr, Nd, and Sm at elevated temperatures (150−250°C), which yielded the corresponding trifluorides.[20]

When CeF_3 is oxidized at RT by F_2 in aHF, CeF_4 is obtained. The reactions of UV-photolyzed F_2 with III/IV mixed oxidation state Pr_6O_{11} or Tb_4O_7 in aHF at RT were reported to produce PrF_4 or TbF_4, respectively, in quantitative yield.[48] Although the results of elemental chemical analysis of so obtained PrF_4 were in agreement with theoretical values, the X-ray powder diffraction analysis done later indicated that sometimes there could be some PrF_3 still present in the final product. When TbF_3 or PrF_3 was used as the starting material, the final products were always LnF_3/LnF_4 mixtures.

4.2 Fluorides of the Main Group Elements

4.2.1 Dioxygenyl Salts

As already shown in the example of O_2AuF_6, various O_2^+ salts can be conveniently prepared by treating gaseous, liquid, or solid fluorides (e.g., AsF_5, BF_3, SbF_5, AuF_3, SbF_3) by UV-photolyzed O_2/F_2 mixtures in liquid aHF at RT. A typical example of the photochemical synthesis of O_2^+ salt in liquid aHF, is the preparation of O_2BF_4 synthesized by reaction between O_2, BF_3, and UV-irradiated F_2 (~1.2 mmol each) in 3−4 mL of liquid aHF.[49] After 12 h of intensive stirring, the volatiles were pumped away at −20°C in dynamic vacuum. Colorless precipitate was recovered from colorless transparent solution. Its Raman spectrum, recorded at RT [1860(100), 1048(5), 767(1009), 727(3), 354(90) cm^{-1}] was in agreement with the formation of O_2BF_4 compound.[49]

The published synthetic attempt (without liquid aHF) of synthesizing O_3^+ salts resulted in synthesis of O_2^+ salts.[50] Therefore it is not expected that the additional use of liquid aHF would change something concerning the preparation of O_3^+ salts.

4.2.2 Xenon

XeF_2 (Xe^{II}) was oxidized by elemental fluorine under UV light in aHF at RT to XeF_4 (Xe^{IV}). Its purity was confirmed by gas-phase IR spectroscopy and by Raman spectroscopy of the isolated solid.[51] When similar syntheses are done with the addition of fluorides (AuF_3, TiF_4, SbF_5, etc.), the oxidation goes further to Xe(VI) yielding XeF_5^+ or $Xe_2F_{11}^+$ salts depending on the starting XeF_6: fluoride ratios.[52] A typical example of such an approach is the preparation of $3XeF_6 \cdot 4TiF_4$ synthesized by the reaction between XeF_2, TiF_4, and UV-irradiated elemental fluorine in aHF at RT.[53] The advantage of this approach is that instead of XeF_6 the solid XeF_2 is used as a starting material and as precursor for the preparation of XeF_6 in situ. The XeF_2/TiF_4 mixtures could be prepared in the requested molar ratio and loaded into reaction vessels in a dry box, whereas the XeF_6 could be added onto TiF_4 only by condensation in a vacuum system. The XeF_2 was converted to XeF_6 by photochemical reaction with UV-irradiated elemental fluorine in liquid aHF at RT. Of course, using XeF_2 or XeF_6 is a matter of choice. For using XeF_2, elemental fluorine, and repeated UV photolysis instead of XeF_6 one pays a stiff price in terms of long reaction times. The crystal structure determination of $3XeF_6 \cdot 4TiF_4$ showed that it can be formulated as $[XeF_5]_3[Ti_4F_{19}]$ consisting from $[XeF_5]^+$ cations and discrete $[Ti_4F_{19}]^{3-}$ anions.

Later, I prepared many other compounds (e.g., $[XeF_5]_2[MnF_6]$, XeF_5MnF_5, $[XeF_5]_4[Mn_8F_{36}]$, $[XeF_5]_5[Ti_{10}F_{45}]$, $[XeF_5][Ti_3F_{13}]$, and $[Xe_2F_{11}]_2[PbF_6]$) and managed to grow corresponding single crystals. Their determined crystal structures still await to be published.

4.2.3 The Rest of the Main Group Elements

For the preparation of binary and ternary fluorine compounds of main group elements, various well-established routes exist that do not require the use of liquid aHF or UV-irradiated F_2. However, few examples can be found in the literature, and some experiments were done by myself, which I would like to mention in this paragraph. The alkali metals, barium, strontium, calcium, and thallium are soluble in aHF with evolution of H_2 and formation of corresponding binary fluorides.[54] Other metals do not dissolve in aHF, although those with standard electrode reductive potentials below

H_2 develop a protective coating of an aHF-insoluble metal fluoride on the surface, e.g., magnesium. At elevated temperatures (180−500°C), Group III (B, Al, Ga, In, Tl), Group IV (Si, Sn Ge, Pb), and Group V (P, As, Sb, Bi) elements react with gaseous aHF yielding binary fluorides.[20]

It was reported that TlF_3 was formed by passing of fluorine, diluted with N_2, through a solution of thallium(I) fluoride. Even though a large excess of F_2 was used, much of the TlF failed to react.[39] SnF_2 is readily soluble in aHF at 20°C. Such solution was found to react smoothly with F_2 ($p < 1$ bar) to yield in aHF-insoluble mixed oxidation state Sn_3F_8 rather expected SnF_4.[55] However, my experiments showed that with larger amounts of F_2 (i.e., higher pressure of F_2), SnF_2 can be quantitatively converted to the Sn(IV) compound SnF_4.

An interesting case represents the chemistry of bismuth. Fluorination of Bi metal with elemental F_2 in aHF at RT results in gray-white Bi(III) compound BiF_3.[26] When powdered Bi is completely covered by liquid aHF, the reaction proceeds smoothly because the released heat is efficiently removed by aHF. The problem arises when some particles of Bi metal are left on the reaction vessel walls above liquid aHF. When they come in contact with elemental fluorine, the reaction is very vigorous and releases a lot of heat in very short time in a single spot on the inner wall of the reaction vessel. As a consequence, the reaction vessel wall becomes very soft on a very small surface area and it cannot resist anymore to overpressure inside the reaction vessel resulting in an explosion.

As found later by me, further reaction of BiF_3 with UV-irradiated F_2 in aHF at RT resulted only in partial oxidation of Bi(III) to Bi(V) yielding an aHF-insoluble colorless product close to the composition $BiF_3 \cdot BiF_5$. It can be also be prepared by direct reaction between BiF_3 and BiF_5 (molar ratio 1:1) in aHF at RT. When BiF_3: BiF_5 starting molar ratios are 2:1 or 1:2, the BiF_3 or BiF_5, respectively, are detected by Raman spectroscopy and X-ray powder diffraction analysis in the recovered products. The Raman spectrum of photochemically prepared $BiF_3 \cdot BiF_5$ [585(100), 537(10), 496(8), 310(1), and 235(5) cm^{-1}] is significantly different from that of BiF_5 [595(100), 570(10), 255(10), 167(5) cm^{-1}][56] and is similar to that of the product obtained by reaction between BiF_5 and H_2O_2.[57] In some experiments I observed the presence of O_2BiF_6/$O_2Bi_2F_{11}$ (very intense vibrational bands at 1848 and/or 1852 cm^{-1} in Raman spectra) in the isolated $BiF_3 \cdot BiF_5$. This must be due to the contamination by oxygen. Without knowing the crystal structure of $BiF_3 \cdot BiF_5$ it is not possible to say if this compound could be formulated as ionic $[BiF_2][BiF_6]$ or more plausible as $BiF_3 \cdot BiF_5$ adduct. The studies of $SbF_3 \cdot SbF_5$ system showed that such systems can be very complex.[58]

5. Conclusions

The described fluorinations by elemental F_2 in aHF, and the photochemical syntheses of binary, ternary, and quaternary compounds using UV-photodissociated F_2 in liquid aHF, offer a milder approach for the formation of these compounds at ambient temperature. All reactions are carried out in reaction vessels made of fluorinated polymers, which are very resistant and inert materials, and therefore there is no danger of final product contamination by by-products formed between the reagents and reaction vessel material. This possibility should be taken into account when metal reaction vessels and very high temperatures are involved. Other advantages of such reactions in aHF are (1) courses of reactions can be visually followed (change in color, dissolution, precipitation, etc.), (2) fluorination can be easily controlled by step-by-step addition of fluorine, and (3) very homogeneous products with small uniform particle size are obtained. If there is a need, various very pure fluorides can be prepared in large quantities. This was, for example, necessary when the influence of cointercalated HF on the electrochemical behavior of highly fluorinated graphite was studied,[59] when reactions between C_{60} and d-block metal fluorides were investigated,[60] when gaseous products of thermal decomposition of some transition metal complex fluorides were studied by high-temperature mass spectroscopy,[61] etc.

One of the obstacles of photochemical reactions is moisture or oxygen contamination, which in many cases results in the formation of undesired by-products (i.e., O_2^+ salts),[62] especially in attempts to prepare binary fluorides. The presence of oxygen can be avoided or reduced by "freeze-pump-thaw-stirring" procedure. The reaction vessel with the sample is frozen at 77 K by liquid nitrogen. The volatiles are pumped away on a vacuum line. The valve is closed, the reaction vessel is warmed up to RT, and the reaction mixture is thoroughly stirred to force gases bubble out. Then the whole procedure is repeated by freezing the reaction vessel, etc.[15]

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