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Chapter 7

NOBLE-GAS FLUORIDES

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Introduction

From what was undoubtedly the first attempt made to induce a reaction between fluorine and a noble gas (1895), Henri Moissan concluded: "A la température ordinaire ou sous l'action d'une étincelle d'induction un mélange de fluor et d'argon n'entre pas en combinaison" [1]. Although the result was disappointing, Ramsay's promptness in supplying Moissan with a sample of argon so soon after its discovery (1894) [2] was an impressive testimony to his chemical awareness. Others also thought of attempting combination of halogens with noble gases in the 1930s, among them Pauling. He was convinced that xenon and fluorine, at least, should react and, at his suggestion, Yost and Kaye tried a discharge experiment*. Their failure to gain a definitive result [3] was cruelly unfortunate since, exposure of xenon–fluorine mixtures to sunlight instead of electric discharge, when tried some 30 years later, produced XeF_2 [4] (see Fig. 7.1). Albeit, it was the observation of the extraordinary oxidising power of PtF_6, by virtue of its ability to oxidise molecular oxygen to O_2^+, and the recognition by Bartlett that xenon should be similarly oxidised because its first ionisation potential is just less than that of O_2, which ultimately led to the discovery of noble-gas compounds. Bartlett showed that PtF_6 oxidises gaseous xenon spontaneously to give a yellow-orange solid [5] (Fig. 7.2). This discovery was greeted with an immediate, world-wide flurry of research activity. Within months, Claassen, Selig and Malm synthesised XeF_4 [6], and a group under Hoppe reported XeF_2 [7]. Noble-gas chemistry was underway!

Isolable compounds are formed only with the heavier gases, krypton and xenon. Work with radon has been limited by its intense radioactivity. The only stable compounds which can be made by direct synthesis are the fluorides. Most compounds involve bonds to the most electronegative elements (fluorine and oxygen), but species with bonds to chlorine, nitrogen and carbon are also known.

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*On 12th July, 1933, in a letter written to Fred Allen to thank him for xenon he had supplied for Yost and Kaye's experiment, Pauling wrote, "I am sorry that the experiments have turned out this way since I felt confident that xenon would combine with fluorine at any rate".

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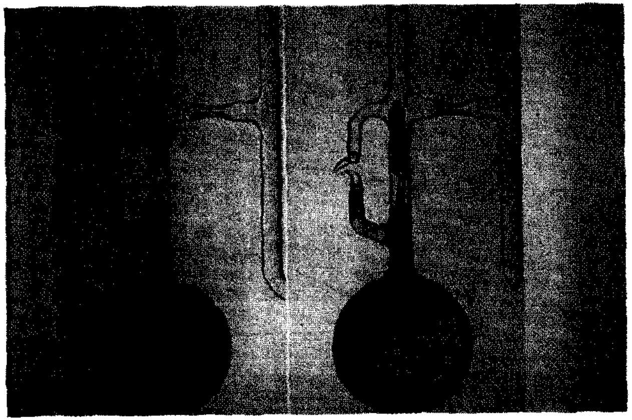
7.1.

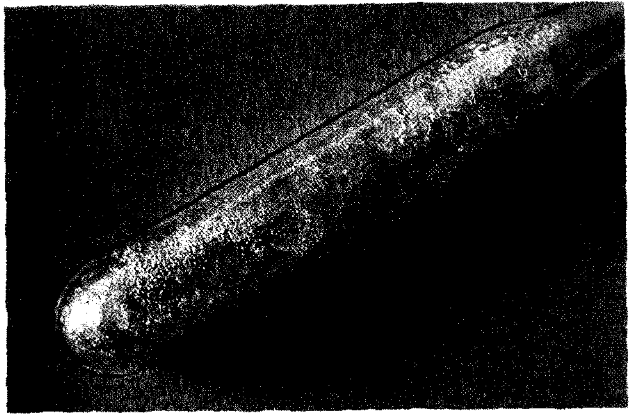
Fig. 7.1. The author with a bulb containing crystals of xenon difluoride produced by sunlight photolysis. (Photograph by courtesy of Dr. L. Stein.)



7.2.

Fig. 7.2 (a) A bulb containing PtF_6 solid and vapour. (b) The same bulb containing an orange-yellow solid after xenon gas had been admitted to the bulb containing the PtF_6. (Photograph by courtesy of *Scientific American* and the Argonne National Laboratory.)

7.3.



7.4.

Fig. 7.3. The first photograph of xenon fluoride crystals obtained at Argonne National Laboratory (under blue illumination). (Photograph by courtesy of *Scientific American* and Argonne National Laboratory.)

Fig. 7.4. A sample tube containing $[Xe]_2^+$ in the presence of $XeF_2 \cdot 2SbF_5$.

Compounds of xenon [8]

The fluorides; their structures and properties

The chemistry of xenon is by far the most extensive. Oxidation states range from +2 to +8 and there is a rich variety of stereochemistries. If only the nearest-neighbour atoms are counted, then xenon is known with all coordination numbers from 0 to 8. Apart from XeF, which has been obtained as an unstable free radical, there is no evidence of odd oxidation-state fluorides.

The three fluorides, XeF_2, XeF_4 and XeF_6, can be obtained by direct reaction of xenon and fluorine. Reports of XeF_8 have not been confirmed. The difluoride is best prepared by heating an excess of xenon with fluorine or by irradiating mixtures of the gases with UV light (or sunlight), the tetrafluoride by heating xenon and fluorine under pressure in a ratio of 1:5 by volume, while the hexafluoride is produced if the ratio is increased to 1:20. The products of the thermal reactions are never free from other xenon compounds. All are colourless solids (Fig. 7.3) but XeF_6 is yellow in the liquid and gaseous states. The di- and tetra-fluorides have low volatilities, and linear and square-planar structures in the solid and vapour states, respectively. The hexafluoride has a higher vapour pressure and its structure has been the source of considerable debate. Unlike other hexafluorides, it is not octahedral in the vapour state but appears to be a non-rigid (floppy) distorted octahedron [9]. As a liquid and in solution the monomer is in equilibrium with tetrameric rings composed of $[XeF_5]^+$ and F^- ions, but at low temperatures the monomer disappears. The fluorines in the $([XeF_5]^+F^-)_4$ tetramers take part in a complex scrambling mechanism as though each of the four units is linked as a cogwheel to its neighbours [10]. In the solid at least four forms exist, but only the cubic modification (which consists of associations of $[XeF_5]^+$ and F^- ions grouped in tetramers and hexamers) has been described in detail [11].

Reactions of the fluorides

All of the chemistry of xenon stems from reactions of the binary fluorides. These fall, essentially into four classes: (i) fluorination reactions; (ii) hydrolysis reactions and reactions yielding oxides, oxide fluorides and oxygen-containing salts; (iii) substitution reactions; and (iv) reactions with fluoride-ion acceptors or fluoride-ion donors.

Fluorination reactions

The difluoride is an excellent mild fluorinating agent of wide application in inorganic [12] and organic [13] chemistry. The tetra- and hexafluorides are progressively more powerful and difficult to control. Soluble in water, the difluoride is stable in neutral or acid solution and powerfully oxidising, converting $2Cl^-$ to Cl_2, Cr^{III} to Cr^{VI} and even $[BrO_3]^-$ to $[BrO_4]^-$. The tetra- and hexa-fluorides are instantly and sometimes dangerously hydrolysed by water (see below).

Hydrolysis reactions and reactions yielding oxides, oxide fluorides and oxygen-containing salts

Although stable in acid and neutral solution in water, XeF_2 decomposes instantly in base with the liberation of xenon, oxygen and HF. The tetrafluoride is instantly hydrolysed by water and, depending on the conditions, up to one-third of the xenon may be retained in solution and XeF_2 may also be liberated. Current thinking [14] suggests that the initial product may be $XeOF_2$ and that this decomposes to give XeF_2 if the water supply is limited. Larger amounts of water may facilitate formation of XeO_2 and XeO which, in turn, may give rise to XeO_3. Control of the vigorous reaction of XeF_6 with water can be achieved by passing dry nitrogen over crystalline XeF_6 to sweep the vapour into water:

$$XeF_6 + 3\,H_2O \longrightarrow XeO_3 + 6\,HF$$

Thus both XeF_4 and XeF_6 hydrolyse to yield the trigonal pyramidal XeO_3 in solution. This aqueous solution is quite stable and is known as 'xenic' acid, but solid XeO_3 is a sensitive and highly dangerous explosive.

In aqueous solution XeO_3 is a powerful oxidising agent, but is kinetically slow. Addition of alkali yields 'xenate' ions $[HXeO_4]^-$, and although salts have been obtained the solutions tend to disproportionate to yield the 'perxenate' ion $[XeO_6]^-$ and xenon:

$$2\,[HXeO_4]^- + 2\,OH^- \longrightarrow [XeO_6]^{4-} + Xe + O_2 + 2\,H_2O$$

The perxenate salts, containing octahedral $[XeO_6]^{4-}$, are powerful and speedy oxidising agents.

Addition of solid Ba_2XeO_6 to cold concentrated H_2SO_4 produces a second xenon oxide, XeO_4, which is an unstable and explosive gas. Understandably, little experimental work has been undertaken with this compound, but it is known to possess a tetrahedral molecular structure.

Although $XeOF_2$, $XeOF_4$, XeO_2F_2 and XeO_3F_2 are all known, the most stable and most studied is $XeOF_4$. A colourless, volatile liquid with a square-pyramidal structure, it is derived from the controlled hydrolysis of XeF_6:

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2\,HF$$

This hydrolysis proceeds further to XeO_3 readily, and the intermediate, XeO_2F_2, is best obtained by the reaction:

$$XeO_3 + XeOF_4 \longrightarrow 2\,XeO_2F_2$$

Not a reaction to be undertaken lightly! The analogous, and possibly more hazardous reaction with XeO_4 yields XeO_3F_2:

$$XeO_4 + XeF_6 \longrightarrow XeO_3F_2 + XeOF_4$$

Substitution reactions [12]

Substitutions on xenon fluorides began with studies of reactions of XeF_2 with anhydrous oxygen-containing acids:

$$XeF_2 + HL \longrightarrow F{-}Xe{-}L + HF$$

$$XeF_2 + 2\,HL \longrightarrow L{-}Xe{-}L + 2\,HF$$

In all cases the linkage to xenon is via oxygen ($L = OTeF_5$, $OSeF_5$, OSO_2F, $OPOF_2$, ONO_2, $OClO_3$, $OCOCH_3$ or $OCOCF_3$). Only the species containing the highly electronegative $-OTeF_5$ and $-OSeF_5$ groups are stable. The $-OSO_2F$ derivatives decompose readily and the rest are explosive.

Analogous derivatives of Xe^{IV} and Xe^{VI} are also unstable and extension of the chemistry into this area has been achieved mainly through the use of the reagent $B(OTeF_5)_3$. The only Xe^{IV} compound known is the solid $Xe(OTeF_5)_4$, while Xe^{VI} gives $Xe(OTeF_5)_6$, $OXe(OTeF_5)_4$ and, under certain conditions in solution, the related partially substituted derivatives. Xenon hexafluoride also reacts with $HOSO_2F$ to give $[XeF_5]^+[SO_3F]^-$ which, although ionic in the solid state and in solution, is also volatile.

Although noble-gas chemistry is concerned mostly with Xe—F and Xe—O bonds, an Xe—N bond has been produced by the replacement of fluorine with another highly electronegative group, $-N(SO_2F)_2$ [15]:

$$XeF_2 + HN(SO_2F)_2 \xrightarrow[0\,°C:\ 4\,d]{in\ CF_2Cl_2} F{-}Xe{-}N(SO_2F)_2$$

The product, once formed, is a rather stable solid which contains a linear F—Xe—N group and a planar arrangement about the nitrogen [15, 16]. Its reaction with AsF_5 yields the solid $[(FSO_2)_2N{-}Xe{-}F{-}Xe{-}N(SO_2F)_2]^+[AsF_6]^-$.

The Xe—C bond has also, apparently, been synthesised by plasma-induced reaction of XeF_2 vapour with $CF_3\cdot$ radicals. The volatile, waxy, white solid product, which decomposes to give XeF_2 and carbon fluorides, is thought to be $Xe(CF_3)_2$ [19].

Reactions with fluoride-ion acceptors or fluoride-ion donors [17]

Known complexes can be classified as derivatives of binary fluorides or oxide fluorides according to the following scheme:

$$XeF_2 \longrightarrow [XeF]^+;\ [Xe_2F_3]^+$$

$$XeF_4 \longrightarrow [XeF_3]^+$$

$$XeF_6 \begin{array}{l} \longrightarrow [XeF_5]^+;\ [Xe_2F_{11}]^+ \\ \xrightarrow{\qquad\qquad\qquad\qquad} [XeF_7]^-;\ [XeF_8]^{2-} \end{array}$$

$$XeOF_4 \begin{array}{l} \longrightarrow [XeOF_3]^+ \\ \xrightarrow{\qquad\qquad\qquad\qquad} [XeOF_5]^-;\ [Xe_3O_3F_{13}]^- \end{array}$$

$$XeO_2F_2 \begin{array}{l} \longrightarrow [XeO_2F]^+ \\ \xrightarrow{\qquad\qquad\qquad\qquad} [XeO_2F_3]^- \end{array}$$

$$XeOF_2 \xrightarrow{\qquad\qquad\qquad\qquad\qquad} [XeOF_3]^-$$

Additionally, there are other more unusual entities such as $[Xe_2]^+$ or $[XeO_3X]^-$ (X = F, Cl or Br). The formulation of many of the complexes as ionic salts is an oversimplification. This is especially true of xenon difluoride adducts.

Reactions with fluoride-ion acceptors – Xenon difluoride has a more extensive fluoride-ion donor chemistry than XeF_4. It reacts with the pentafluorides of arsenic, antimony and bismuth, and a large range of transition-metal pentafluorides, to give adducts which can be thought of as $[XeF]^+[M_2F_{11}]^-$, $[XeF]^+[MF_6]^-$ and $[Xe_2F_3]^+[MF_6]^-$ formulations in which the cation units are linked to the counterion forming F—Xe····F····M chains; the V-shaped $[Xe_2F_3]^+$ ion itself can be regarded as two $[XeF]^+$ units linked by a fluorine bridge. Complexes with MOF_4 ($M = W$ or Mo) are similar.

Originally formulated as $Xe^+[PtF_6]^-$, this first noble-gas compound has since been shown to have the variable composition $Xe(PtF_6)_x$ ($x = 1 - 2$), and it is uncertain whether Xe^+, $[Xe_2]^+$ or $[Xe_2F]^+$ are involved or whether it can be more correctly represented in terms of $[XeF]^+[PtF_6]^-$ and $[XeF]^+[Pt_2F_{11}]^-$. The complexes of XeF_2 with $XeOF_4$ and with the halogen pentafluorides are certainly not of this type but are molecular adducts.

An interesting reaction of $[XeF]^+[Sb_2F_{11}]^-$ is its reduction with H_2O or certain other reductants which give rise to the bright-green paramagnetic cation $[Xe_2]^+$ (Fig. 7.4), which can also be obtained by oxidation of xenon with dioxygenyl salts.

Xenon tetrafluoride forms complexes with only the strongest fluoride-ion acceptors (SbF_5 and BiF_5), but XeF_6 has an extensive and complex chemistry in which it forms 1:1 and 2:1 adducts with a variety of penta-, tetra- and tri-fluorides. Solutions of XeF_6 in HF compared with those of XeF_2 and XeF_4 have a high conductivity because of the occurrence of both $[XeF_5]^+$ and $[Xe_2F_{11}]^+$ ions in solution:

$$([XeF_5]^+F^-)_4 + n\,HF \rightleftharpoons 2\,[Xe_2F_{11}]^+ + [(HF)_nF]^-$$

$$[Xe_2F_{11}]^+ + n\,HF \rightleftharpoons 2\,[XeF_5]^+ + [(HF)_nF]^-$$

and it is these same two ions which are found in the adducts. The $[XeF_5]^+$ ion has the same square-pyramidal structure as is found in XeF_6 itself. The best description of $[Xe_2F_{11}]^+$ is in terms of an ionic description, $[XeF_5]^+F^-[XeF_5]^+$, but with a measure of covalent character in terms of ($[XeF_5]^+XeF_6$) to explain the non-linearity of the Xe—F—Xe bonds.

Xenon oxide tetrafluoride is a relatively poor fluoride-ion donor and, consequently, complexes only with strong Lewis acids. Thus with SbF_5, $[XeOF_3]^+[Sb_2F_{11}]^-$ and $[XeOF_3]^+[SbF_6]^-$ have been obtained. Similarly, XeO_2F_2 yields $[XeO_2F]^+[Sb_2F_{11}]^-$ and $[XeO_2F]^+[SbF_6]^-$ but these are less stable. Raman and NMR spectroscopy have established their ionic nature, and shapes consistent with those expected from VSEPR theory are found.

Reaction of $FXeOTeF_5$ with AsF_5 has given $[XeOTeF_5]^+[AsF_6]^-$, which undergoes interesting reactions, during the course of which a number of as yet uncharacterised xenon cations are formed.

Reactions with fluoride-ion donors — Fluoride-ion acceptor behaviour is confined to XeF_6 which reacts with alkali-metal fluorides to form $MXeF_7$ (M = Cs, Rb) and M_2XeF_8 (M = Cs, Rb, K and Na) which lose XeF_6 when heated. The thermal stability of these adducts increases with increasing molecular weight, the M_2XeF_8 (M = Cs and Rb) compounds decomposing only above 400 °C. The sodium complex, however, decomposes below 100 °C, providing a convenient means of separating XeF_6 from XeF_2 and XeF_4 with which it does not react. No solid-state structures have been determined, but complexes of NOF and NO_2F have also been obtained and $[NO]_2^+$ $[XeF_8]^{2-}$ has been shown to contain a slightly distorted square-antiprismatic $[XeF_8]^{2-}$ ion. There is no clear evidence for a ninth coordination position for the lone pair, this seemingly being in violation of VSEPR theory.

Evaporation of mixtures of appropriate amounts of solutions of XeO_3 and MF gives the stable, white solids $nM^+[XeO_3F]_n^-$, in which the anion consists of chains of pseudo-octahedral xenon atoms linked by angular bridges. The haloxenates $CsXeO_3Cl$ and $CsXeO_3Br$ have also been obtained.

Anions from the unstable oxide fluorides $XeOF_2$ and XeO_2F_2 have been derived from solutions of $XeOF_2$ and CsF in anhydrous HF. Either $CsXeOF_3$ or $CsXeO_2F_3$ is obtained depending on the conditions under which the solvent is removed.

Complexes of $XeOF_4$ with CsF, RbF, KF and NOF have been known for some time. The caesium salts, $CsF \cdot 3XeOF_4$, $CsF \cdot XeOF_4$, $3CsF \cdot 2XeOF_4$ and $3CsF \cdot XeOF_4$, for example, are obtained by treating the alkali fluorides with an excess of $XeOF_4$ and pumping to constant weight at appropriate temperatures. The structure of the stable $CsF \cdot XeOF_4$ complex has been shown to contain an $[XeOF_5]^-$ anion of distorted octahedral geometry, the lone pair of electrons apparently occupying an octahedral face. The $CsF \cdot 3XeOF_4$ complex contains the $[F(XeOF_4)_3]^-$ anion which consists of three $XeOF_4$ units, which have close to square-pyramidal structure linked via three $Xe \cdots F$ bonds to a common fluorine [18].

Compounds of radon and krypton [8, 17]

Stable compounds of helium, neon and argon are not known, although experimental estimates of the bond strength in $[ArF]^+$ suggest that continued effort to lock it into an adduct is worthwhile. Radon appears to form a difluoride and complexes in halogen fluorides which probably contain $[RnF]^+$. The case for the existence of $[RnF]^+$ has also recently been strengthened by the observation of the formation of a non-volatile product from the reaction of radon with solid $[O_2]^+[SbF_6]^-$. The assumed reaction is:

$$Rn(g) + 2\,([O_2]^+[SbF_6]^-(s)) \longrightarrow [RnF]^+[Sb_2F_{11}]^-(s) + 2\,O_2(g)$$

The chemistry of krypton is less extensive than that of xenon. Small amounts of the violet free radical KrF have been observed during the γ-radiation of KrF_2, but most of the chemistry is concerned with the difluoride and its derivatives. Early reports of the preparation of KrF_4 have not been confirmed.

The volatile, colourless, crystalline solid KrF_2 is best made by subjecting mixtures of krypton and fluorine, cooled to −186 °C, to an electric discharge or irradiating liquid krypton fluorine mixtures with UV light. It has the same linear molecular structure as XeF_2. Because of its low bond energy, it is a very powerful fluorinating agent capable of oxidising iodine to IF_7 and xenon to XeF_6 at room temperature. It is also rapidly decomposed by water without requiring the addition of a base.

Complexes of KrF_2 are similar to those of XeF_2 and are limited to cationic species formed with fluoride-ion acceptors. Thus compounds of the types $[Kr_2F_3]^+[MF_6]^-$ (M = As, Sb and Ta), $[KrF]^+[MF_6]^-$ (M = As, Sb, V, Ta, Pt and Au) and $[KrF]^+[M_2F_{11}]^-$ (M = Sb, Nb and Ta) are known in the solid state and in solution, and more recently compounds such as $[KrF]^+$-$[MOF_5]^-$ (M = Mo and W) and its relatives have been prepared and characterised by NMR and Raman spectroscopy. The spectra of the ions correlate well with those of the xenon analogues, but additional peaks in the Raman spectra of $[Kr_2F_3]^+$ indicate that the cation is unsymmetrical. The oxidising power of $[KrF]^+$ and $[Kr_2F_3]^+$ is even greater than that of KrF_2, capable of oxidising IF_5 to $[IF_6]^+$, O_2 to O_2^+, Xe to $[XeF_5]^+$, BrF_5 to $[BrF_6]^+$ and Au to $[AuF_6]^-$ and AuF_5.

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BIOGRAPHIC NOTE

John Holloway was born in Ashby-de-la-Zouch in England in 1938. He gained his B.Sc. and Ph.D. degrees at the University of Birmingham. As Assistant Lecturer and Lecturer he established an inorganic fluorine research group in Aberdeen, Scotland, beginning in 1963. During the period 1963 - 70 he spent two years at Argonne National Laboratory in the U.S.A. He joined the staff of the University of Leicester in 1971, where he is now Senior Lecturer in Chemistry. He was awarded the D.Sc. degree in 1976. (See Fig. 7.1., page 150).