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RECENT ADVANCES IN NOBLE-GAS CHEMISTRY

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I. Introduction

Until "$XePtF_6$" was reported in 1962 (*1*), the only compounds containing noble-gas elements in combination with other elements were weakly bonded species of two main types: (i) gaseous cationic or excited-state species observed by spectroscopic means and (ii) species in which the noble-gas atoms are adsorbed, enclathrated, or encapsulated on or within the lattices of other molecules. The former includes mostly excited-state diatomic molecules containing like or unlike noble-gas atoms, or diatomics containing oxygen, nitrogen, or metal atoms in combination with a noble-gas atom, a wealth of van der Waals–bonded dimers and trimers, diatomic cationic species containing like or unlike noble gases, or noble-gas hydrides. These were briefly reviewed in 1968 (*2*). The latter consists mainly of clathrates in which the noble-gas atoms lie at the interstices of crystalline cages formed by water, organic molecules, or double hydrates involving both organic and water molecules [e.g., species such as $R \cdot 2Ng \cdot 17H_2O$ ($R = CH_3COOH$, CH_2Cl_2, $CHCl_3$ or CCl_4, and Ng = Ar, Kr, or Xe)] (*2–4*), or where noble-gas encapsulation in zeolites occurs (*4*).

Subsequent to the discovery of the xenon–platinum hexafluoride

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complex, simple binary fluorides of xenon (XeF_2, XeF_4, and XeF_6), krypton (KrF_2), and radon (probably RnF_2), have been prepared (*2–4*), and the general chemistry of these species has been well established and developed. Compounds isolable at ordinary temperatures have been obtained only for the heavier noble gases, and the only stable compounds that can be made by direct synthesis are the fluorides. Most of the compounds that have been obtained consist of the noble gas combined with the most electronegative elements, fluorine and oxygen. However, compounds in which the noble gases are bonded to nitrogen, carbon, or chlorine have been characterized, and there is a growing and interesting chemistry evolving around some of these species. The chemistry of xenon is undoubtedly the most extensive, xenon occurring in oxidation states +2 to +8, and stable species have been isolated for each of these. For krypton and radon, the compounds found so far are all in oxidation state +2 and, until quite recently, all of the known species involved only krypton-to-fluorine or radon-to-fluorine bonds. The most sensitive detection methods have provided no definitive evidence for a stable argon compound. The inert status for helium and neon remains unchallenged.

The chemistry of xenon stems from the reactions of the binary fluorides and falls into five main categories:

1. reactions in which the xenon fluoride acts as a fluorinating agent,
2. hydrolysis reactions yielding oxide fluorides, oxides, and oxygen-containing salts,
3. fluoride/anion metathesis reactions between the fluoride and an anhydrous acid,
4. reactions with fluoride ion acceptors, yielding fluorocations, and
5. reactions with fluoride ion donors, yielding fluoroanions.

Krypton chemistry parallels that of xenon but is, in general, more limited. The bonds between krypton and other elements, even the highly electronegative fluorine and oxygen atoms, are weaker than those with xenon. The outcome is that although krypton–fluoride cationic species are known, Kr–O, Kr–N, and Kr–C bonds are difficult to obtain and, where they exist, are unstable. On the other hand, the weakness of the Kr–F bond, both in neutral KrF_2 and in the cations $[KrF]^+$ and $[Kr_2F_3]^+$, provides a means of carrying out useful low-temperature fluorinations, which have been exploited in producing novel species that are often inaccessible using elemental fluorine.

Radon apparently forms a difluoride and some cationic complexes. However, the evidence is based exclusively on radiochemical tracer experiments because radon has no stable isotopes, and the work is made even more difficult by radon's intense radioactivity, which not only makes it hazardous to manipulate but also leads to decomposition of the reagents involved.

A wealth of reviews covering various aspects of noble-gas chemistry were written up to the end of 1979 and some of those written in English are listed in reference (*5*). In addition to the books (*2*, *3*) and an extensive and authoritative book chapter (*4*) already mentioned, three other books appeared in the early days of noble-gas chemistry, and these are listed in reference (*6*). There is also a valuable and authoritative bibliography covering the literature in the period 1962 to 1977 (*7*).

Because the main features of noble-gas chemistry are now well documented to the extent that they appear in all undergraduate inorganic textbooks, this review concerns itself only with the new chemistry that has evolved since 1979, and an effort has been made to pick out the main features of this work and set it within the context of the chemistry established up until that time.

II. Recent Review Literature

Since 1979, there have been a number of reviews of note. Among them is an interesting summary of the history of the discovery of noble-gas chemistry in which the reasons for the failure of Yost and Kaye to obtain noble-gas compounds in the 1930s are examined. The article also speculates whether there were others who envisioned noble-gas reactivity and discusses work that took place before Bartlett's key experiments (*8*). Other general summaries of noble-gas chemistry were published in celebration of the 25th anniversary of the discovery of chemical activity of xenon, at the 100th anniversary of the discovery of fluorine (*9*) and very recently in a new "Encyclopaedia of Inorganic Chemistry" (*10*). A review covering aspects of the chemistry of xenon, and especially its reactions with pentafluoro-oxoselenate and pentafluoro-oxotellurate groups, was published at the beginning of the review period (*11*), and a detailed and comprehensive academic review of cationic and anionic complexes of the noble gases was published in 1984 (*12*). An important development in noble-gas chemistry over the last 15 years has been the synthesis of compounds containing stable bonds between noble gases and elements other than fluorine and oxygen. This was foreseen in an article in 1982, which traced then-recent developments and discussed Xe–N bonding as well as the fragmentary evidence for Xe–C and Xe–B bonds (*13*).

An authoritative review on the chemistry of radon, which includes the formation of clathrate compounds, the simple and complex fluorides, ionic radon in solution, redox properties, and the various unsuccessful efforts to prepare an oxide and halides of radon other than the fluoride, was published by the most significant contributor to this field in 1983 (*14*).

A review article on van der Waals complexes of metal–atom noble-gas complexes was published in 1995 (*15*).

III. The Possibility of Argon Chemistry

The existence of krypton and xenon compounds inevitably raises the question as to whether noble-gas chemistry might be extended to argon. The increasing range of krypton compounds that have been synthesized over the last 10 years, and in particular the recent observation of Kr–O and Kr–N species, will undoubtedly further stimulate interest in this area.

Although some years ago *ab initio* calculations on $[HeF]^+$ and $[NeF]^+$ indicated that the ground states of these molecules are unstable, those for $[ArF]^+$ implied a stable ground state and suggested that a likely complex to be synthesized would be $[ArF]^+[PtF_6]^-$ (*16*). Evidence from photoelectron spectroscopy did indeed produce evidence of $[ArF]^+$ and provided a measure of its dissociation energy $\{D_0([ArF]^+) \geq 1.655\ \mathrm{eV}\}$ but confirmed instability for the helium and neon analogs (*17*). More recently new *ab initio* calculations at the MP4(SDTQ)/6-311G(2df, 2pd)//MP2/6-31G(d, p) level predict that the best counterions for the stabilization of $[ArF]^+$ appear to be $[AuF_6]^-$ or $[SbF_6]^-$ (*18*). High-level calculations also predict that $[HC{\equiv}N{-}ArF]^+$ should be stable with a binding energy of 160 $\mathrm{kJ \cdot mol^{-1}}$ which is closely similar to that of the recently observed krypton analog $[HC{\equiv}N{-}KrF]^+$ (157 $\mathrm{kJ \cdot mol^{-1}}$) (*19*). Interesting work, in which electronegativity has been redefined and adjustments to the well-established electronegativity scales have been made, has demonstrated close agreement between the four scales (Allred and Rochow, Sanderson, Mulliken, and Pauling) and that the values for argon and krypton are similar (*20*). All of this suggests that more effort to prepare an argon fluoride complex might be worthwhile.

IV. Krypton Chemistry

The chemistry of krypton is less extensive than that of xenon, and the well-established characteristics, summarized in detail in the book chapters in 1973 by Bartlett and Sladky (*4*) and in 1984 by Selig and Holloway (*12*) are dealt with in outline here, but the new developments since 1979 are referenced in detail.

The only stable binary fluoride of krypton is the difluoride, KrF_2, and all the known chemistry derives from this molecule. Early reports of the preparation of KrF_4 have not been substantiated, and no simple stable oxides or oxide fluorides have been isolated. However, small amounts of the violet free radical, KrF, have been observed following γ-irradiation of KrF_2 (*2–4*). There has also now been direct observation of $[KrO_n]^+$ ($n = 1, 2$) and $[KrOH]^+$ by Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry, for which *ab initio* theoretical calculations suggest that the two species are covalently bonded with bond dissociation enthalpies of 237.7 and 169.5 $kJ \cdot mol^{-1}$ respectively (*21*).

The volatile, colorless crystalline difluoride was prepared initially by subjecting mixtures of krypton and fluorine at low temperature and pressure to an electric discharge or by irradiation of liquid krypton/fluorine mixtures with UV light (*22*). The latter is a more rapid and convenient way of preparing KrF_2 than the earlier discharge method, and it has since been found that laser as well as UV photolysis is also effective (*23*). These photolytic methods are particularly useful for preparing small quantities (*22, 23*). Because molecular fluorine is not significantly dissociated until 500–600°C, the preparation of thermally unstable compounds such as KrF_2 by a thermal method did not seem to be an option. However, in 1976, Soviet workers reported the preparation of KrF_2 using catalytic–thermal generation of atomic fluorine from molecular fluorine (*24*). The nonequilibrium conditions necessary were created by generating atomic fluorine on the surface of a nickel wire at 600–700°C and allowing the atomic fluorine to react with krypton in a low-temperature zone close to the reactor wall at −196°C. The rate of production is high (~6 g/h) compared with other preparative methods. The reaction method and operating conditions of another high-yield, thermal catalytic method has also recently been discussed (*25*).

Krypton difluoride has now been shown to exist in two crystallographic forms, a low-temperature (−196°C) phase, referred to as α-KrF_2, and a high-temperature (−78°C) phase, β-KrF_2 (*23*). Study of the vibrational spectra has shown that the X-ray structure reported in 1972 (*26*), which contains two linear KrF_2 molecules per tetragonal unit cell (space group $P4_2/mnm$) aligned in planes perpendicular to the tetrad axis, is that of β-KrF_2. Raman data suggests that the α-KrF_2 crystallizes in the same space group as XeF_2 (*27*), but a definitive conclusion must await an X-ray structural investigation of the krypton species at low temperature.

The adducts of KrF_2 are analogous to those of XeF_2 and until quite recently were limited to cationic derivatives, $[KrF]^+$, $[KrF]^+ \cdot xKrF_2$, $[Kr_2F_3]^+$ or $[Kr_2F_3]^+ \cdot KrF_2$, of Lewis acid pentafluorides (*12, 28*) or the related but somewhat less powerfully Lewis acidic metal oxide tetrafluorides (*12, 28, 29*). More recent reports have included the synthesis of $[KrF]^+[MF_6]^-$ (M = As, Sb) in anhydrous HF (*30*), the preparation of $[KrF]^+[As_2F_{11}]^-$ for the first time, and the observation of two solid-state forms of $[KrF]^+[Sb_2F_{11}]^-$ (*23*), providing only the second example of polymorphism in krypton complex chemistry {*cf.* $[KrF]^+[AsF_6]^-$ (*31*)}. The cationic complex of krypton difluoride, $[Kr_2F_3]^+ \cdot xKrF_2 \cdot [BF_4]^-$, incorporating the $[BF_4]^-$ anion, has been prepared for the first time from the reaction of KrF_2 with BF_3 at −40°C in HF. The presence of HF to help bring about the ionization was shown to be essential in this preparation because the complex is not produced at temperatures as low as −78°C when KrF_2 and BF_3 are brought directly together (*30*). The use of anhydrous HF has also provided a means of synthesizing two new metal fluoride adducts, $2KrF_2 \cdot MnF_4$ and $KrF_2 \cdot MnF_4$, from the combination of KrF_2 and MnF_2 in HF solvent (*32*). The 2:1 adduct decomposes in dynamic vacuum at −45°C, yielding KrF_2 and the 1:1 adduct, which itself is stable up to −25°C. Because neither species provided a Raman spectrum, their exact nature is uncertain, but it seems likely that they are molecular adducts rather than complexes with cationic/anionic character.

In general, the component molecules of all of the cationic/anionic complexes are linked together by fluorine bridges, which have a considerable degree of ionic character. However, Raman spectra of the complexes derived from the metal oxide tetrafluorides indicate that they are best formulated as essentially covalent structures (*12*). The spectra of the $[Kr_2F_3]^+$ cation correlate well with those associated with the analogous xenon species, but additional peaks, which have no equivalents in the xenon spectra, indicate that, unlike $[Xe_2F_3]^+$, the krypton cation is unsymmetrical (Fig. 1) with one short and strong bond, $Kr_a–F_a$, a weaker and longer bond, $Kr_b–F_c$, and two bridging bonds, Kr_b---F_b and Kr_a---F_b, which are also of different lengths and strengths (*31*). Alternatively, the cation may be regarded as a dis-

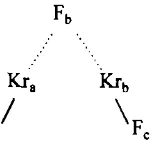


FIG. 1. The structure of $[Kr_2F_3]^+$.

torted KrF_2 molecule fluorine bridged to a $[KrF]^+$ cation, $[KrF_2 \cdot KrF]^+$ (*33*).

As in the case of xenon, one of the most interesting developments in krypton chemistry has been the identification of bonds between noble-gas atoms and elements other than fluorine. The first example of such a species containing a Kr–O bond, $Kr(OTeF_5)_2$, has been prepared by the reaction of krypton difluoride with $B(OTeF_5)_3$ at −90 to −112°C in SO_2ClF solvent (*34*), the thermally unstable product decomposing to species analogous to those found in the decomposition of $Xe(OTeF_5)_2$. The high solubility of $B(OTeF_5)_3$ relative to KrF_2 in SO_2ClF at the low temperatures required for the stabilization of $Kr(OTeF_5)_2$ is thought to serve to maintain $B(OTeF_5)_3$ in excess and to prevent the formation of $FKr(OTeF_5)$, which was not observed (*34*).

Perhaps even more remarkable is the extension of krypton chemistry to include Kr–N-bonded species in the cations $[HC{\equiv}N{-}KrF]^+$ (*35*) and $[R_fC{\equiv}N{-}KrF]^+$ ($R_f = CF_3, C_2F_5, n\text{-}C_3F_7$) (*36*). The first to be prepared, the fluoro(hydrocyano)krypton(II) cation, $[HC{\equiv}N{-}KrF]^+$, was obtained from the low-temperature reaction of KrF_2 with $[HC{\equiv}NH]^+[AsF_6]^-$ in HF or BrF_5 solvent rather than by direct combination of $[KrF]^+[AsF_6]^-$ with $HC{\equiv}N$ in HF or BrF_5 (which was the route used in the preparation of the xenon analog) because, not only is $[KrF]^+$ strongly oxidizing toward $HC{\equiv}N$ and BrF_5, it also tends to undergo autoredox reactions in both solvents (*35*). Warming of $[HC{\equiv}N{-}Kr{-}F]^+[AsF_6]^-$ in BrF_5 solution to −58 to −55°C for several hours produced little evidence of decomposition, but brief warmings above −50°C led to rapid formation of $[NF_4]^+$, CF_4, and CF_3H. However, when the solid complex is warmed above −50°C, krypton, NF_3, and CF_4 gases are rapidly evolved. Extension of the HCN work to include other nitrogen bases that are oxidatively resistant and have first adiabatic ionization potentials close to or exceeding that of $[KrF]^+$ has led to the preparation of three other examples of cationic Kr–N-bonded species. Derived from perfluoroalkyl nitriles, these species, $[R_fC{\equiv}N{-}KrF]^+[AsF_6]^-$ ($R_f = CF_3, C_2F_5, n\text{-}C_3F_7$), have been prepared by reaction of $R_fC{\equiv}N/AsF_5$ mixtures with KrF_2 in BrF_5 at temperatures between −57 and −61°C, and have been compared with their xenon analogs, which have also been made (*36*).

Inevitably, the discovery of the krypton–nitrogen-bonded species has led to the testing of a number of theoretical models. Nonrelativistic quantum chemical calculations, including electron correlation effects, have been done for the ground-state $[HC{\equiv}N{-}KrF]^+$ cation, and the computed geometrical structure, stability toward dissociation, and harmonic vibrational spectrum agree closely with the experimental data (*37*, *38*). The calculations suggest a Kr—F bond stronger than that in KrF_2. The fact that the xenon analog was also made prompted a comparison of the experimental properties of the bonds formed between nitrogen and fluorine to the noble gas atoms, which suggested that the exceptional ability of the $[NgF]^+$ (Ng = Kr, Xe) ions to act as Lewis acids is related to the presence of holes in the valence shell charge concentrations of the krypton and xenon atoms, which expose their cores. The study also provided reason to believe that the mechanism of formation of the Ng–N bonds in the adducts is similar to that in the formation of hydrogen bonds (*39*).

The ability of noble-gas fluorides to bring about oxidation and/or fluorination is in the order $XeF_2 \approx$ covalent Xe(II) derivatives $< XeF_4 < XeF_6 < KrF_2$. Also, it is well known that the cationic derivatives, $[XeF]^+$, $[Xe_2F_3]^+$, $[XeF_3]^+$, $[XeF_5]^+$, $[Xe_2F_{11}]^+$, and $[KrF]^+$ or $[Kr_2F_3]^+$ have a higher fluorinating ability than their neutral parent compounds (*13*). Clearly, from this comparison, it is evident that KrF_2 and its cationic derivatives are the most powerful noble-gas fluorinating agents. Indeed, thermodynamic data indicate that reactions involving KrF_2 are about 50.2 $kJ{\cdot}mol^{-1}$ more exothermic than those with elemental fluorine. This has two consequences: the first is that such reactions have to be undertaken with great care; the second is that these reagents offer the potential to synthesize other novel high-oxidation-state species (*13*). This important characteristic has been exploited for some time. For example, KrF_2 is known to fluorinate xenon to XeF_6 and iodine to IF_7 (*33*), whereas the $[KrF]^+$ cation reacts spontaneously with oxygen to yield $[O_2]^+$ and xenon to give $[XeF]^+$ (*31*). The cations, $[KrF]^+$ and $[Kr_2F_3]^+$, oxidize BrF_5 to $[BrF_6]^+$ [*40, 41*]. The fact that $[KrF]^+$ takes BrF_5 to $[BrF_6]^+$ but fails to take $XeOF_4$ to $[XeOF_5]^+$ (*42*) has been explained in terms of the $[KrF]^+$ attacking BrF_5 at the bromine because of the nucleophilic attraction of its nonbonding lone pair whereas the most nucleophilic part of the $XeOF_4$ molecule is its oxygen atom. Thus, an intermediate XeF_4–OF might be expected (*43*). This is given further credence by the observation of a yellow explosive intermediate in reactions of $[KrF]^+$ with

$XeOF_4$ (*44*). It is also noteworthy that $XeOF_4$ is not fluorinated by PtF_6 (*45*).

The successful oxidation of BrF_5 to $[BrF_6]^+$ led to investigations on the oxidative fluorination of metals and metal fluorides. The first example was the successful oxidation of elemental gold to gold(V) (*42*), the treatment of Au powder in anhydrous HF giving a pale yellow solid, $[KrF]^+[AuF_6]^-$, which is sparingly soluble in HF to give a pale yellow solution:

$$7KrF_2 + 2Au \xrightarrow[\text{aHF}]{20^\circ\text{C}} 2[KrF]^+[AuF_6]^- + 5Kr. \qquad (1)$$

Pyrolysis of the krypton complex at between 60 and 65°C gave gold pentafluoride, AuF_5:

$$[KrF]^+[AuF_6]^- \xrightarrow[8\,\text{h}]{60\text{–}65^\circ\text{C}} AuF_5 + Kr + F_2. \qquad (2)$$

Since then, the oxidative fluorinating abilities of KrF_2 have been used to prepare CoF_3 (*46*), MnF_4 (*32*), and the lanthanum tetrafluorides, LnF_4 (Ln = Ce, Pr, or Tb) (*47*), and their heptafluoro complexes, Cs_3LnF_7 (Ln = Ce, Pr, Nd, Tb, Dy, or Tm) (*47*, *48*). Cobalt trifluoride and the lanthanum compounds can also be prepared using xenon fluorides, except for the thermally unstable PrF_4, which can only be obtained using KrF_2 (*47*). Further careful investigation of the reaction of KrF_2 with LnO_2 (Ln = Ce, Tb, or Pr) in 2 : 1 or 3 : 1 ratios has shown that, here again, LnF_4 is produced, but reaction at a 1 : 1 ratio gives a product with a composition close to that of $LnOF_2$ that has been shown not to be a mixture of LnO_2 and LnF_4 (*49*). Another species in oxidation state four that has been prepared is the hexafluoronickelate(IV) anion, $[NiF_6]^{2-}$, as the $[Xe_2F_{11}]_2^+[NiF_6]^{2-}$ salt, by the reaction of NiF_2, XeF_6, and KrF_2 in anhydrous HF (*50*). Reaction of KrF_2 with $[XeF_5]^+[AuF_4]^-$ in anhydrous HF below 273 K gives $[XeF_5]^+[AuF_6]^-$ (*51*).

A number of high-oxidation-state fluorides and oxide fluorides have also been prepared using KrF_2. For example, CrO_2F_2 can be converted to $CrOF_4$ (*29*) [rather than $CrOF_3$ which is the product of reaction with XeF_2 (*52*)] and has been shown to form a stable 1 : 1 adduct with KrF_2 which has an essentially covalent structure with a $Kr\cdots F\cdots Cr$ bridge (Fig. 2). A notable achievement has been the synthesis of AgF_3 (*53*) by precipitation from anhydrous HF solutions of $[AgF_4]^-$ salts by addition of fluoro acids such as BF_3, PF_5, or AsF_5. It was also shown

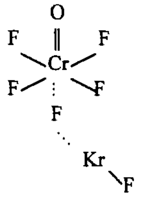


FIG. 2. The structure of $CrOF_4 \cdot KrF_2$.

that previous claims were in fact due to Ag(II)Ag(III)F_5 (*53*). There has also been considerable interest in the derivation of high-oxidation-state fluorides from a number of the actinide oxides or fluorides. Reactions of the oxides and tetrafluorides of uranium, neptunium, and americium, and the oxyfluorides of neptunium, with KrF_2 in BrF_5 or HF were reported in the mid 1970s and early 1980s (*53–55*), and brief mention has been made of the preparation of UF_6 from UF_4 (*56*), the fluorination of $NpOF_4$ to NpF_6 (*57*), and the oxidation of PuF_3 to PuF_4 (*58*) using KrF_2 at room temperature or lower. More recently (*59*), it has been shown that not only uranium and neptunium oxides and low-valent fluorides but also plutonium tetrafluoride can be converted to their hexafluorides at ambient temperature using KrF_2 vapor or KrF_2 in anhydrous HF. However, efforts to prepare AmF_6 from AmO_2 in anhydrous HF failed, in contrast to the earlier report (*55*). The highest oxidation-state species synthesized recently using KrF_2 in anhydrous HF have been $TcOF_5$, made by reaction with TcO_2F_3 (*60*), and the new osmium(VIII) oxide fluoride, *cis*-OsF_4O_2, prepared by the fluorination of OsO_4 (*61*). The latter was previously erroneously characterized as OsF_6O (*62*).

Another interesting aspect of the oxidative fluorinating ability of krypton difluoride is its ability to produce coordinatively saturated fluorocations. By 1974 three such species were known, namely, $[NF_4]^+$, $[ClF_6]^+$, and $[BrF_6]^+$, the last being produced using $[KrF]^+$ or $[Kr_2F_3]^+$ (*41*, *42*). It was later shown that the $[NF_4]^+$ salts could be prepared using the $[KrF]^+$ cation, KrF_2 reacting with NF_3 in the presence of the Lewis acids SbF_5, NbF_5, PtF_5, TiF_4, and BF_3 to yield $[NF_4]^+[SbF_6]^-$, $[NF_4]^+[NbF_6]^-$, $[NF_4]^+[PtF_6]^-$, $[NF_4]^+_2[TiF_6]^{2-}$, and $[NF_4]^+[BF_4]^-$ respectively (*63*). In more recent studies, the syntheses of $[NF_4]^+[SbF_6]^-$, $[NF_4]^+[AsF_6]^-$ (*30*), and $[NF_4]^+[BF_4]^-$ (*25*, *30*) have been studied under different conditions. The fluorination of NF_3 by $[KrF]^+[SbF_6]^-$ in anhydrous HF has been shown to proceed quantitatively at temperatures as low as −31°C, indicating an ionic two-electron mechanism. It was shown that ClF_5 and BrF_5 could also be converted to their complex fluorocations by $[KrF]^+$. In contrast, PtF_6 was shown to be capable of oxidizing only NF_3 and ClF_3 but not BrF_5. Efforts to fluorinate OF_2, CF_3NF_2, and $[ClF_4O]^-$ with $[KrF]^+$ salts, however, were not successful (*30*).

An unusual reaction of KrF_2 has been the observation that KrF_2 decomposes on zeolites at 233 K, fluorinating the zeolite and encapsulating the krypton released. A proportion of the latter is retained even upon heating to 773 K, demonstrating the potential for ^{85}Kr recovery using KrF_2/zeolite systems (*64*). As might be expected, the fluorination of C_{60}-fullerene by KrF_2 is extreme, yielding species ranging from $C_{60}F_{44}$ to the hyperfluorinated species $C_{60}F_{78}$, as determined by mass spectrometry. An interesting observation in these experiments, however, is that in comparison with other fluorination methods, the concentration of oxygen-containing derivatives is low (*65*).

V. Xenon Chemistry

A. CORE CHEMISTRY AND RECENT ADVANCES

With the exception of XeF, which is obtained as an unstable free radical (*2–4*), there is no evidence for the occurrence of xenon compounds in odd-numbered oxidation states. The only species that can be synthesized directly from the elements are the three fluorides XeF_2, XeF_4, and XeF_6. Early reports of the preparation of XeF_8 have not been substantiated.

There are a variety of methods for the preparation of XeF_2 (*2–4*), and recent additions include oxidation of xenon using the blue solutions of AgF_2 in HF (*66*) and a new thermal catalytic synthesis (*25*). The latter is related to that recently devised for the preparation of gram quantities of KrF_2 (*24*) and has the potential to become one of the better methods for producing XeF_2. However, this route in the hands of other workers appears to yield rather pure XeF_6 (*67*), so the conditions need further study and appraisal. In the meantime, the best methods to make the difluoride are by heating an excess of xenon with fluorine (*2–4*) or by irradiating Xe/F_2 mixtures with ultraviolet light or sunlight (*2–4, 68*). Xenon tetrafluoride is the most difficult xenon fluoride to prepare because, even under optimum conditions (heating xenon and fluorine under pressure in a 1:5 ratio), equilibrium concentrations of XeF_2 and XeF_6 occur (*2–4*). The claim that XeF_4, free from contamination by XeF_2 or XeF_6, can be prepared by irradiation of a gaseous mixture of xenon and fluorine (molar ratio

$\geq 1:2$) in a reactor with walls coated with NiF_2 (*69*) is probably not valid. However, the thermal combination of xenon and fluorine in a 1:20 ratio of 350°C for two days followed by one day at 50°C in the presence of sodium fluoride yields mainly the involatile complex, $Na_2[XeF_8]$ [Eq. (3)] but with traces of XeF_2 and XeF_4. After removal of the volatile mixture of XeF_2 and XeF_4, the $Na_2[XeF_8]$ is decomposed at 350°C to give XeF_4 [Eq. (4)] (*70*):

$$Xe + 3F_2 + 2NaF \xrightarrow[50^{\circ}C\,(1\,d)]{350^{\circ}C\,(2\,d)} Na_2[XeF_8] \tag{3}$$

$$Na_2[XeF_8] \xrightarrow{350^{\circ}C} XeF_4 + F_2 + 2NaF. \tag{4}$$

Another route to high-purity XeF_4 that has been discovered recently involves a modification of the thermal catalytic method (*24*) in which the fluorinating agent is O_2F_2 rather than F_2 (*67*).

The best preparative route to XeF_6 remains the thermal combination of xenon and fluorine in a 1:20 ratio at high pressure (*2–4*). However, the thermal catalytic method using elemental fluorine also seems to yield a pure product, albeit in a lower yield (*67*).

All of the xenon fluorides are colorless solids except the hexafluoride, which is yellow in the liquid and gaseous states. The di- and tetrafluorides have low volatility and the expected linear ($D_{\infty h}$) and square planar (D_{4h}) structures respectively in both the solid and vapor states. The bonding in these structures has been accounted for using a three-center, four-electron bond model similar to that employed to explain the structure of CO_2. Although the structures and bonding for XeF_2 and XeF_4 have been widely accepted for many years, physicochemical studies continue to be reported and refinements made. For XeF_2, new Raman spectra in the solid state and vapor phase at 325 K have been reported, and force constants have been evaluated using a SVFF approximation (*71*). Raman study of the molecular dynamics of XeF_2 in acetonitrile (*72*), hydrogen fluoride, and bromine pentafluoride (*73*) (which are the most widely used solvents in noble-gas fluoride chemistry) at various concentrations has been carried out, and vibrational and rotational correlation functions, as well as the characteristic times, have been calculated.

The structure of XeF_6 in the solid, liquid and vapor states continues to be discussed in detail. Out of all the known hexafluorides, it has the highest boiling point, suggesting that, unlike other hexafluorides, it might be polymeric in the liquid and solid states. Some of the uncertainty has arisen because of difficulties in manipulating the compound. Its powerful fluorinating ability leads to it damaging container and window materials and producing lower-xenon fluorides, which contaminate the specimen. Another difficulty is its ready hydrolysis to the dangerously explosive solid, XeO_3. In the vapor state, it has been clear for some time that an octahedral structure for this molecule could not have the lowest energy (*74–76*). The VSEPR model (*74, 75*) predicted that an extra lone pair should be stereochemically active and distort the molecule to lower symmetry. Experimental and theoretical work has demonstrated that this is indeed the case, with the molecule having local minima giving C_{3v} and C_{2v} geometries via a pseudorotation mechanism in which the lone pair moves over the octahedral faces and edges (*77, 78*). Theoretical work in 1987 provided additional information concerning O_h, C_{2v}, and C_{3v} structures (*79*), and more recent experimental work, using high-resolution photoelectron spectroscopy to resolve the ligand field splittings, yielded bond angles for the C_{3v} structure that agreed with the theoretical work (*80*). These studies also confirmed earlier work that indicated that the dipole moment is very small. However, both pieces of work referred to the C_{2v} structure as a local minimum, and no theoretical vibrational frequency analysis was presented to support this. Now, the O_h, C_{2v}, and C_{3v} structures have been studied with a significantly larger basis set, and harmonic vibrational frequencies for each have been determined and analyzed (*81*). At the SCF level of theory, the O_h and C_{2v} structures have been shown not to be minima but to be transition states whose imaginary vibrational frequencies lead to the C_{3v} structure.

Nothing new has emerged recently about the structure of XeF_6 in the liquid state and in solution, and the current state of knowledge was well reviewed by Seppelt and Lentz in 1982 (*13*). In both the molten state and in solution, monomeric XeF_6 is in equilibrium with tetrameric $([XeF_5]^+F^-)_4$ but at low temperatures the monomer disappears. The 25 fluorines of the tetramer are involved in a complex scrambling mechanism, which is perhaps related to that in $Rh_4(CO)_{12}$, although it is clear that no xenon–xenon bonds equivalent to the metal–metal bonds in the rhodium compound occur. In the solid state, at least four phases exist, of which, because of lack of X-ray intensities, absorption problems, and disorder, only the cubic structure, which contains 144 XeF_6 molecules in the unit cell arranged as 24 tetramers and 8 hexamers, has been determined. In each, the fluorines attached to each xenon form square pyramidal configurations, with the remaining fluorine atoms contributing to a twofold or threefold bridge linking adjacent xenons. Because the bridging

F^- ions are not close to the fourfold axis of the $[XeF_5]^+$ groups, it has been suggested that lone pairs of electrons may occupy this position.

Thermochemical data on the xenon fluorides continues to accumulate. New melting and boiling points of XeF_2 at 136 ± 5°C and 338°C respectively, and an enthalpy of fusion of 14.04 ± 2.09 kJ·mol^{-1}, have been obtained, and disproportion of XeF_2 to XeF_4 and Xe has been observed above 350°C (*82*). A new determination of the heat of formation of XeF_2, obtained by the combustion of germanium in the difluoride, is in close agreement with an earlier value obtained by reaction of XeF_2 with PF_3 (*83*). Existing thermodynamic data have been used to calculate successive one-electron potentials for the reduction of XeF_2 (*84*).

From the beginning of noble-gas chemistry there has been continued interest in theoretical and spectroscopic aspects. The more recent include an ESCA study of XeF_2 to high statistics in which the satellites observed on the low-energy side of the xenon 3d and 4d primary photolines have been attributed to monopole transitions from the occupied MOs of XeF_2 to the antibonding and/or Rydberg-state orbitals (*85*). The nature of the satellite lines has been identified using theoretical SCF-Xα-SW calculations. This has been followed up by X-ray photoelectron spectroscopy and theoretical studies on XeF_4 and XeF_6 in which the Xe 4d and Xe 3d spectra have been reported. However, the main center of focus in this paper was on KrF_2 (*86*). Other theoretical work that has been carried out includes SCF-MO studies on XeF_2 and XeF_4 (*87*) and the application of the multiple-scattered-wave-SCF-X_α method to estimate ionization potentials and charge distribution in XeF_2, XeF_4, XeF_6, and $XeCl_2$. The role of 5d orbitals, especially their importance in XeF_4 and XeF_6 binding, has been discussed (*88*).

Many attempts have been made to understand theoretically the electronic structures of XeF_n ($n = 1, 2, 4, 6$) species, the majority having been made since the mid-1970s (*79*, *81*, *89–93*). Generally, these have utilized the conventional Hartree–Fock molecular-orbital approach and in some cases correlation effects have been included (*81*, *89*). Relativistic effects have been ignored despite the fact that, due to the high nuclear charge of xenon, they should be high. The spectra have been studied by different techniques (e.g., *75*, *80*, *94*). Now, all-electron Dirac–Fock and Dirac–Fock–Breit calculations for the series have been caried out, and the role of relativistic effects on bond lengths and dissociation energy has been reported (*95*).

B. REACTIONS OF THE XENON FLUORIDES

With the exception of the reactions of xenon with the powerful fluorinating agent PtF_6 and its relatives, all of the chemistry of xenon has been derived from reactions of the binary fluorides.

1. *Hydrolysis Reactions Yielding Oxide Fluorides, Oxides, and Oxygen-Containing Salts*

All of the known oxides, oxide fluorides and a number of oxygen-containing salts stem from hydrolysis reactions of XeF_4 or XeF_6. It has been well established for some time that no stable oxo-species can be obtained from the difluoride, XeF_2. Stable in acid or neutral solution, it decomposes instantaneously in base with liberation of xenon, oxygen, and hydrogen fluoride. The tetrafluoride, on the other hand, is instantly hydrolyzed by water and, depending on the conditions, up to one third of the xenon may be retained in solution. There is also evidence that some XeF_2 may be liberated. There has been little recent work in this area, but the most recent (*96*) suggests that the initial product may be $XeOF_2$ and that this decomposes to give XeF_2 if the water supply is limited. In the presence of larger amounts of water, XeO_2 and XeO may be produced and in turn can produce XeO_3.

The reaction of XeF_6 with water is difficult to control and can result in explosions. However, the reaction can be controlled by passing dry nitrogen over crystalline XeF_6 at room temperature to sweep the vapor into water, where the following reaction occurs:

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF. \quad (5)$$

Hence, the aqueous hydrolysis of both XeF_4 and XeF_6 results in the formation of the trigonal pyramidal trioxide, XeO_3, in solution. Aqueous solutions of the trioxide, known as "xenic" acid, are fairly stable and can be used as powerful but kinetically slow oxidizing agents. These might have found wide application were it not for the fact that solid XeO_3, which is readily obtained from these solutions on evaporation, is a violent and sensitive explosive.

The addition of alkali to XeO_3 solutions yields "xenate" ions $[HXeO_4]^-$. Although salts of this species can be isolated, solutions containing $[HXeO_4]^-$ disproportionate to give the "perxenate" ion, $[XeO_6]^{4-}$, and xenon:

$$2[HXeO_4]^- + 2[OH]^- \rightarrow [XeO_6]^{4-} + Xe + O_2 + H_2O. \quad (6)$$

Within the time frame of this review, an improved synthesis of perxenate solutions has been devised in which XeF_6 is dissolved in excess of $HOPOF_2$ under carefully controlled conditions, the excess of $HOPOF_2$, HF, and OPF_3 is removed, and the XeO_3 remaining is dissolved slowly in 4 M NaOH at 0°C (*90*). Both reactions have been carried out on the 6- to 7-mmol scale without explosions occurring.

The addition of solid Ba_2XeO_6 to cold concentrated sulfuric acid yields a second xenon oxide, XeO_4, as an unstable and explosive gas. Not surprisingly, this has been little studied, but infrared spectroscopy and electron diffraction have shown that it has the expected tetrahedral geometry.

The controlled hydrolysis of XeF_6 with water in a 1:1 molar ratio produces the colorless, stable, volatile liquid $XeOF_4$, which has a square pyramidal structure:

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF. \qquad (7)$$

Efforts to produce XeO_2F_2 by the addition of a further stoichiometric quantity of water have resulted only in the production of XeO_3, and no evidence for a dioxide difluoride intermediate has ever been obtained.

Of the known oxide fluorides, $XeOF_2$, $XeOF_4$, XeO_2F_2, and XeO_3F_2 (*2–4*, *96*), the most stable is $XeOF_4$. The monoxide difluoride, $XeOF_2$, mentioned earlier, is unstable but can be obtained from the reaction of XeF_4 with water at −80°C. The dioxide difluoride is obtained by mixing XeO_3 with $XeOF_4$ at dry-ice temperature and fractionally distilled from the resulting mixture of XeO_2F_2, $XeOF_4$, and XeF_2. Although thermodynamically unstable with respect to XeF_2 and O_2, it is sufficiently stable to be held in well-fluorinated Kel-F containers for several days. The trioxide difluoride can be obtained by reaction of XeF_6 with either XeO_4 or $Na_4[XeO_6]$ but is contaminated with other xenon species, principally $XeOF_4$ (*3*, *4*, *96*). The reactions of xenon fluorides and oxide species have been systematized in order of descending acidity, $XeF_6 > XeO_2F_4 > XeO_3F_2 > XeO_4 > XeOF_4 > XeF_4 > XeO_2F_2 > XeO_3 \approx XeF_2$ (*97*).

The most recent advances in this area include new syntheses of $XeOF_4$ by the reaction of $NaNO_3$ (*98*) [Eq. (8)] or POF_3 (*99*) with a very slight excess of XeF_6. In the case of the former, an excess of $NaNO_3$ has to be avoided to suppress the secondary reaction (*98*) [Eq. (9)], whereas in the latter, excess of POF_3 may lead to generation of explosive XeO_3 (*99*):

$$NaNO_3 + XeF_6 \rightarrow NaF + XeOF_4 + FNO_2 \quad (8)$$

$$NaNO_3 + XeOF_4 \rightarrow NaF + XeO_2F_2 + FNO_2. \quad (9)$$

Reaction of $CsNO_3$ with a large excess of XeF_6 at temperatures above the melting point of XeF_6 proceeds quantitatively according to Eqs. (10) and (11) to yield $XeOF_4$ (*100*). However, if in Eq. (10) the excess of XeF_6 is reduced to less than 100%, some of the CsF can react with $XeOF_4$ to yield $Cs^+[XeOF_5]^-$. For this and other reasons, substitution of $CsNO_3$ by $NaNO_3$ is advantageous (*98*, *100*). The reaction of $CsNO_3$ with an excess of $XeOF_4$ yields FNO_2 and XeO_2F_2 in quantitative yield with CsF and $CsXeOF_5$ as by-products. Provided an excess of $XeOF_4$ is used, a better new and safe synthesis for XeO_2F_2 is the reaction of $XeOF_4$ with N_2O_5 (*100*):

$$CsNO_3 + XeF_6 \rightarrow CsF + XeOF_4 + FNO_2 \quad (10)$$

$$CsF + XeF_6 \rightarrow CsXeF_7. \quad (11)$$

New chemistry of $XeOF_4$ and XeO_2F_2 includes the preparation of a series of novel pentafluoro-orthotellurate derivatives (*101*). Reaction of XeO_2F_2 with $B(OTeF_5)_3$ according to Eq. (12) has yielded the previously unknown compound $O_2Xe(OTeF_5)_2$:

$$XeO_2F_2 + 2B(OTeF_5)_3 \rightarrow 3O_2Xe(OTeF_5)_2 + 2BF_3. \quad (12)$$

However, with excess of XeO_2F_2, a mixture of $O_2Xe(OTeF_5)_2$, $O_2XeF(OTeF_5)$ and XeO_2F_2 was produced.

There has been very little new information on xenic and perxenic acids and their salts since the late 1960s. More recent information includes study of the spectra and protolytic properties of aqueous perxenic acid in the pH range −0.2 to 13, which yielded p*K* values at 25°C as follows:

$$pK_{H_4XeO_6} < 0; \qquad pK_{[H_3XeO_6]^-} = 4.29 \pm 0.03; \qquad pK_{[H_2XeO_6]^{2-}} = 10.81 \pm 0.04.$$

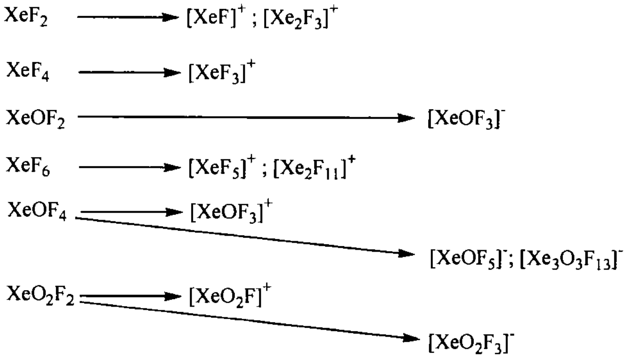
The enthalpy of dissociation of $[H_3XeO_6]^-$ at 25°C is $0 \pm 5\ kJ \cdot mol^{-1}$ and that of $[H_2XeO_6]^{2-}$ is $3 \pm 2\ kJ \cdot mol^{-1}$ (*102*). The participation of 5d orbitals in the bonding of high-valent oxygen compounds, including $[HXeO_4]^-$ and $[XeO_6]^{4-}$, has also been investigated by examination of the $K_{\alpha 1}$ and $K_{\beta 1}$ X-ray emission lines in these ions (*88*).

2. *Reactions with Fluoride-Ion Donors and Acceptors*

A major part of the chemistry of xenon fluorides and oxide fluorides is associated with their reactions with fluoride donors and acceptors to produce a variety of cations and anions. The known species are summarized in Scheme 1. In addition, there are a number of more unusual entities, notably the dixenon cation $[Xe_2]^+$ and $[XeO_3X]^-$ (X = F, Cl, or Br). The preparations, structures, and chemistry of these species was comprehensively reviewed in 1984 (*12*), so only developments since 1979 are covered in this present account.

It is important to remember that the formulation of many of these species as salts is an oversimplification. In general, most are essentially fluorine bridged but with a high degree of ionic character. Also, there are a number of adducts, such as $XeF_2{\cdot}XeF_4$ and $XeF_2{\cdot}IF_5$, whose overall formulas are suggestive of donor–acceptor species, which are simple molecular adducts.

a. Xenon Cations The transient green coloration observed in the early days of noble-gas chemistry was identified in 1978 as being due to the dixenon cation (*103*, *104*). The cation can be produced either by oxidation of gaseous xenon using $[O_2]^+$ or by reduction of $[XeF]^+$ with water or other reducing agents such as lead or mercury. The green species is stable in SbF_5 indefinitely at room temperature under an atmosphere of xenon gas (*103–105*). Now, almost 20 years after the initial characterization of $[Xe_2]^+$ (*103*), a structural characterization of $[Xe_2]^+[Sb_4F_{21}]^-$ has shown that the Xe–Xe bond is weak and longer, at 3.087(1) Å, than any other main-group element bond observed so far (Fig. 3). It has also been shown that the presence of HF in the SbF_5 is essential (i.e., no reaction of $[XeF]^+[Sb_2F_{11}]^-$ with Xe



SCHEME 1. Major cationic and anionic derivatives of xenon fluorides and oxide fluorides.

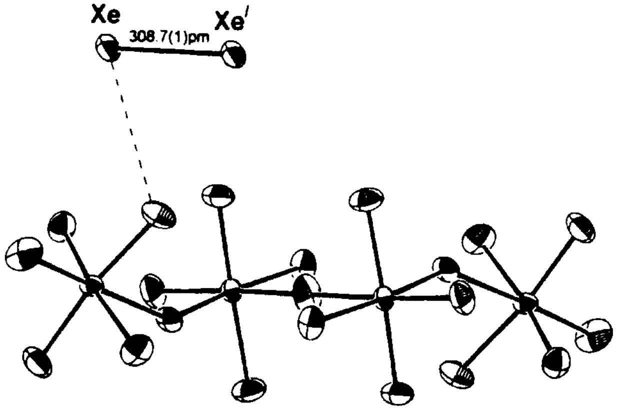


FIG. 3. The structure of $[Xe_2]^+[Sb_4F_{21}]^-$. [Reprinted with permission from (*106*); copyright 1997 VCH Verlagsgesellschaft mbH.]

occurs in the presence of HF-free SbF_5), and it is speculated that the ion $[Xe(HF)_2]^{2+}$ is the active oxidizing agent in the $Xe/XeF_2/SbF_5/HF$ system (*106*).

One piece of recent chemistry of $[Xe_2]^+$ has been its reaction with bromide and iodide ions in the presence of xenon gas, which yields the excited complexes XeBr* and XeI* respectively (*107*).

Xenon difluoride has an extensive fluoride-ion donor chemistry, which is exemplified by its reaction with a large range of transition metal pentafluorides to give adducts formulated as $[XeF]^+[M_2F_{11}]^-$, $[XeF]^+[MF_6]^-$, and $[Xe_2F_3]^+[MF_6]^-$ in which the cations and anions are linked by weak fluorine bridging bonds, F—Xe---F---M. The V-shaped $[Xe_2F_3]^+$ cation is symmetrical, two $[XeF]^+$ units being linked by a fluorine bridge. Related complexes incorporating the weaker Lewis acids, MOF_4 (M = W or Mo), are similar but have less ionic character. Essentially, no new chemistry has been derived in this area since publication of the review by Selig and Holloway in 1984 (*12*). However, it has been shown that $[N_2F]^+[AsF_6]^-$ will oxidize xenon to $[XeF]^+$ (*108*). On the theoretical front, the electronic structures and bonding in the $[Xe_2F_3]^+$ cation and the unknown but isoelectronic and isostructural neutral species $XeIF_3$ (i.e., $[FXeFXeF]^+$ and FXeFIF respectively) have been calculated using *ab initio* molecular orbital theory with polarized split-valence basis sets (*109*). The $[Xe_2F_3]^+$ cation is known to be bent at the central fluorine, but the calculated structure is linear and the bonds from the xenons to the central fluorine are 0.09 Å shorter than the experimentally determined values. The calculated vibrational frequencies are in reasonable agreement with experimental values after scaling. The $[Xe_2F_3]^+$ cation is a good example of a 5c, 6e hypervalent bond; for $XeIF_3$, the bonding is less delocalized but the components of the six-electron (5c, 6e) hypervalent bond are still present.

In accord with enthalpy of ionization data, xenon tetrafluoride forms complexes with only the strongest fluoride-ion acceptors, but XeF_6 has a much more extensive and complicated chemistry, forming 1:2, 1:1, 2:1, and 4:1 adducts with a variety of tri-, tetra- and pentafluorides that incorporate $[XeF_5]^+$ or $[Xe_2F_{11}]^+$ cations. Solutions of the hexafluoride in anhydrous HF have a higher conductivity than those of XeF_2 and XeF_4 because of the occurrence of both of these cations in solution (*12*):

$$([XeF_5]^+F^-)_4 + n\text{HF} \rightleftharpoons 2[Xe_2F_{11}]^+ + [(HF)_n]^- \qquad (13)$$

$$[Xe_2F_{11}]^+ + n\text{HF} \rightleftharpoons 2[XeF_5]^+ + [(HF)_nF]^-. \qquad (14)$$

Work that was not covered in the 1984 review (*12*) or has appeared since includes preparation of 1:1 complexes with LnF_3 (Ln = La, Pr, or Nd), which, upon thermal decomposition, gave rise to the adducts $2LnF_3 \cdot XeF_6$ and $3LnF_3 \cdot XeF_6$. The stabilities of the 1:1 and 2:1 complexes appeared to decrease with increasing atomic number of the lanthanide (*110*). Reactions with tin and lead tetrafluorides have given the adducts $XeF_6 \cdot 4MF_4$, $3XeF_6 \cdot 4MF_4$, $4XeF_6 \cdot MF_4$ (M = Pb, Sn), and $4XeF_6 \cdot 3SnF_4$ for the first time (*111*). The 1:4 adducts contain $[XeF_5]^+$ cations and polymeric anions, and the 4:1 complexes contain $[Xe_2F_{11}]^+$ cations. The complexes with 4:3 and 3:4 stoichiometries are novel and are the first xenon hexafluoride complexes that contain both $[Xe_2F_{11}]^+$ and $[XeF_5]^+$ cations. More recent work from the same group on the $4XeF_6 \cdot NiF_4$ species is the first to have shown definitively the presence of two $[Xe_2F_{11}]^+$ cations in the same compound. The complex, prepared from the reaction of NiF_2, KrF_2, and XeF_6 in anhydrous HF, is therefore formulated as $[Xe_2F_{11}]_2^+[NiF_6]^{2-}$ (*50*). It has also been shown that displacement of BrF_3 from $BrF_3 \cdot AuF_3$ with XeF_6 gives $[XeF_5]^+[AuF_4]^-$, which is isostructural with $[XeF_5]^+[AgF_4]^-$, the structure of which contains double layers of $[XeF_5]^+$ and layers of $[AgF_4]^-$ with all the layers parallel to the *ab*-plane. The greater basicity of $[AuF_4]^-$ relative to that of $[AgF_4]^-$ implies that the ligand charge in the gold anion should be higher than that in the silver salt. This appears to be confirmed by the difference in the unit cells of the two salts and is consistent with observed differences in the basicity and oxidizability of the anions (*51*).

Work on species incorporating metal pentafluorides includes data on $2XeF_6 \cdot VF_5$, which had been reported earlier, and the novel complexes $XeF_6 \cdot nVF_5$ ($n = 1$ or 2). This Raman study suggested that ionic character decreases from essentially ionic to molecular in the order $2XeF_6 \cdot VF_5$, $XeF_6 \cdot VF_5$, $XeF_6 \cdot 2VF_5$ (*112*). More recently, the first BiF_5 complex, the white diamagnetic solid $[XeF_5]^+[BiF_6]^-$, has been obtained. This exhibits a strong fluorine-bridge interaction between the cation and anion, which distorts the anion from O_h symmetry (*113*). Further detailed studies on the interpretation and assignment of vibrational spectra have been reported by two independent workers (*114*, *115*).

Adducts of XeF_2 with $[XeF_5]^+$ salts were first examined in 1971 (*116*), but to obtain a firmer understanding of the factors that determine adduct formation and to investigate the possibility of lower fusion temperatures, the phase diagram for the $XeF_2/[XeF_5]^+[AsF_6]^-$ system has been studied and representative structures of the $XeF_2:[XeF_5]^+[AsF_6]^-$ products (1:2, 1:1, and 2:1) have been carried out by X-ray single-crystal methods (*117*). Whether the complexes are polymeric or nonpolymeric is correlated with the coordination number of the $[XeF_5]^+$ cations in the complexes, and this is determined by the extent of ionization of the XeF_2 species.

There has been significant interest in the problems associated with heptacoordination in recent years [see (*118*) references 1–11], and although $[XeF_7]^+$ has not been synthesized, its possible existence is of major interest in this context. Recent *ab initio* calculations employing effective core potentials and density functional theory calculations have been used for analysis of the isoelectronic series $[TeF_7]^-$, IF_7, and $[XeF_7]^+$. These show that all three possess a pentagonal bipyramidal equilibrium geometry and that $[XeF_7]^+$ is a stable structure. However, it is conceded that the synthesis of such a species is likely to be very difficult because its calculated oxidized strength is closely similar to that of $[KrF]^+$ (*118*).

Xenon oxide tetrafluoride is a poorer fluoride ion donor than XeF_2 and XeF_6, and therefore complexes only with the stronger Lewis acids. Thus, although $[XeOF_3]^+[SbF_6]^-$ and $[XeOF_3]^+[Sb_2F_{11}]^-$ have been known for some time (*12*), the first single-crystal structure determination of the $[XeOF_3]^+$ cation was obtained on the $[XeOF_3]^+[SbF_6]^-$ salt more recently. As expected, the isolated cation has a geometry that is consistent with VSEPR theory. Oxygen-17 and -18 enrichment of the $[XeOF_3]^+$ cation in HF and SbF_5 solvents has allowed comprehensive investigation of the ^{17}O and ^{129}Xe nuclear magnetic resonance of the cation (*119*). Xenon dioxide difluoride yields

$[XeO_2F]^+[SbF_6]^-$ and $[XeO_2F]^+[Sb_2F_{11}]^-$, but these too are somewhat unstable, the cation decomposing slowly in SbF_5 according to Eq. (15) (*12*):

$$[XeO_2F]^+ \xrightarrow[r.t.]{SbF_5} [Xe\text{-}F]^+ + O_2. \qquad (15)$$

However, the reaction of XeO_2F_2 with excess of AsF_5 in anhydrous HF has been shown to yield the $[XeO_2F]^+[AsF_6]^-$ species, which has a dissociation pressure of 7 torr at 23°C. Under vacuum or when exposed to a laser beam, this loses AsF_5 to give $[FO_2XeFXeO_2F]^+[AsF_6]^-$. This same species can also be prepared by reaction of XeO_2F_2 with AsF_5 in a 2:1 molar ratio in anhydrous HF. A detailed Raman study of the two adducts has shown that, whereas the $[FO_2XeFXeO_2F]^+$ $[AsF_6]^-$ species has minimal interaction between the anion and cation, the $[XeO_2F]^+[AsF_6]^-$ species is significantly fluorine bridged (*120*).

b. Anions Derived from Xenon Fluorides and Oxide Fluorides Fluoride ion acceptor behavior among the xenon fluorides has, until the late 1980s, been limited to XeF_6. Reactions of the alkali metal fluorides with XeF_6 yield M_2XeF_8 (M = Cs, Rb, K, or Na) and $M'XeF_7$ (M′ = Cs or Rb), which lose XeF_6 when heated. The thermal stability of the adducts increases with increasing relative molecular mass, and the decomposition temperature of the sodium complex, which is below 100°C, provides a means of separating XeF_6 from XeF_2 and XeF_4 (see Section V,A). The related NOF and NO_2F adducts have also been prepared, and the NOF derivative $[NO]_2^+[XeF_8]^{2-}$ was shown some years ago to contain a slightly distorted square antiprismatic $[XeF_8]^{2-}$ anion (*12*). More recently, it has been demonstrated that XeF_6 also reacts with $[NF_4]^+[HF_2]^-$ in anhydrous HF to give $[NF_4]^+[XeF_7]^-$, which undergoes laser photolysis at 488 nm to yield the $[NF_4]_2^+[XeF_8]^{2-}$ complex. Vibrational spectroscopic data on these two complexes, along with those of the previously prepared cesium salts, and evidence for the existence of $NaXeF_7$ have been obtained (*121*). The $[NF_4]^+[XeF_7]^-$ salt is by far the most energetic of the known $[NF_4]^+$ salts, and a DSC study of its decomposition has provided a means of calculating its heat of formation ($\Delta H_f^\circ = -490.7\ kJ \cdot mol^{-1}$) (*122*). The most important and most recent work in this area, however, is the X-ray structural analyses of $Cs^+[XeF_7]^-$, $[NO_2]^+[Xe_2F_{13}]^-$ (*123*), and $Cs_2^+[XeF_8]^{2-} \cdot 4BrF_5$ (*124*). Prepared from the reaction of XeF_6 with CsF in BrF_5 at 4°C, the anion in $Cs^+[XeF_7]$ is a capped octahedron, a geometry strictly enforced by the symmetry constraints of the cubic lattice.

This, of course, is at variance with most other seven-coordinate main-group compounds, which are pentagonal bipyramidal. The bond from xenon to the capping fluorine is long (210 pm) compared with the average of the rest of the xenon–fluorine bonds ($Xe{-}F_{Oh}$ = 195 pm). This may be a consequence of interaction between $Xe{-}F_{cap}$ and the nonbonding electron pair, or it may arise from interaction with three cesium cations (the other fluorines have contacts to only two cations). The anion in $[NO_2]^+[Xe_2F_{13}]^-$ can be considered as an adduct of an $[XeF_7]^-$ anion with a discrete XeF_6 molecule (Fig. 4). This is the first structure in which distinct XeF_6 as opposed to $[XeF_5]^+F^-$ units have been observed. The $[XeF_7]^-$ adopts a capped trigonal prismatic arrangement in which the $Xe{-}F_{cap}$ bond is the shortest and the lone pair appears to be between the two Xe–F bonds *trans* to $Xe{-}F_{cap}$. The XeF_6 part of the adduct has C_{2v} symmetry, with two short, two intermediate, and two long Xe–F bonds, and so is significantly distorted from the regular octahedral structures exhibited by the isoelectronic $[IF_6]^-$ and $[SeF_6]^{2-}$ anions (*123*). In the BrF_5-solvated $Cs_2^+[XeF_8]^{2-}$ complex (*124*), the anion assumes the near-regular square antiprismatic structure found in $(NO)_2^+[XeF_8]^{2-}$ (*125*). This structure is related to that of $[IF_8]^-$, but the Xe–F bonds are longer. This can be explained in terms

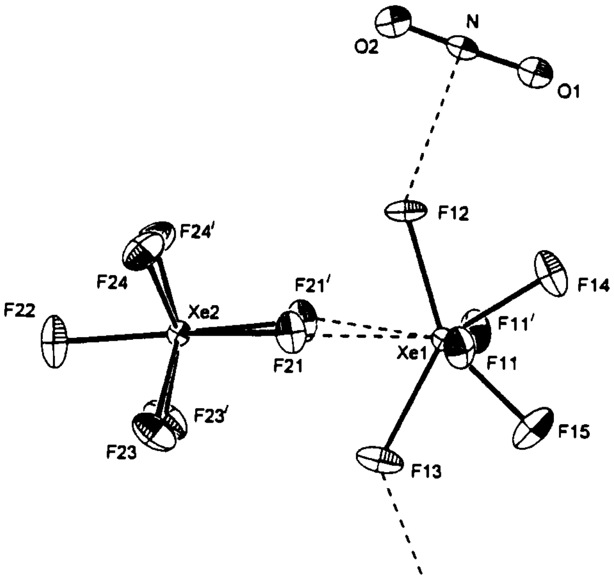
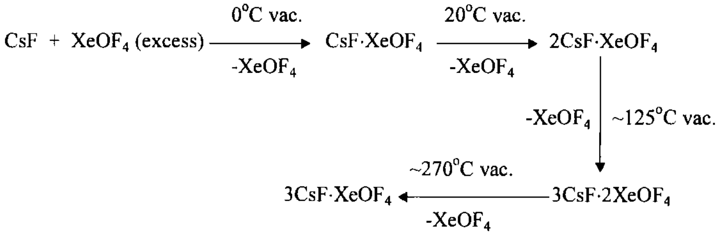


FIG. 4. The structure of $[NO_2]^+[Xe_2F_{13}]^-$, showing the disposition of the $[XeF_7]^-$ and discrete XeF_6 molecule and the $[NO_2]^+$. [Reprinted with permission from (*123*); copyright 1996 VCH Verlagsgesellschaft mbH.]

of shielding by the centrosymmetric nonbonding electron pair or by increased polarity of the Xe–F bonds due to the increased negative charge.

The first evidence of possible fluoride-ion-acceptor behavior of XeF_4 was from reports of the synthesis of $M_2^+[XeF_6]^{2-}$ (M = Cs, Rb, K, Na) salts from the reaction of XeF_4 with MF (*126–128*). The characterization of these species as $[XeF_6]^{2-}$ salts was based on vibrational spectra (*128*), which were later shown to be incompatible with those for an octahedral species (*129*). Furthermore, the Raman spectrum attributed to the cesium salt was found to be identical to that due to a species observed during the laser photolysis of $Cs^+[XeF_7]^-$ and tentatively assigned to $Cs_2^+[XeF_8]^{2-}$ (*121*). These discrepancies prompted an investigation of the reactions of XeF_4 with $N(CH_3)_4F$, which is a powerful reagent in the synthesis of complex fluoroanions, and a reexamination of the XeF_4/MF systems, which has led to the identification and full characterization of $[XeF_5]^-$ for the first time (*130*). Direct reaction of excess of XeF_4 with the alkali-metal fluorides, MF (M = Cs, Rb, K, Na) at 190°C and reaction of equimolar amounts of XeF_4 with $N(CH_3)_4F$ in CH_3N at −40°C or of XeF_4 with excess of FNO at 0°C gave the 1 : 1 complexes. Detonation of $[N(CH_3)_4]^+[XeF_5]^-$ in CH_3CN when cooled with liquid nitrogen can occur, and $[NO]^+[XeF_5]^-$ is unstable, with a dissociation pressure of 10 torr at 0°C, but the alkali metal salts are stable, as was found in the earlier work (*126–128*). All of the salts were characterized by vibrational, ^{19}F, and ^{129}Xe NMR spectroscopy, and an X-ray single-crystal structure determination was carried out on $[N(CH_3)_4]^+[XeF_5]^-$. The structure contains planar $[XeF_5]^-$ anions of D_{5h} symmetry in which all six atoms are coplanar. The results from the structure and from a normal coordinate analysis indicate a greater rigidity of the XeF_5 plane than that in the fluxional IF_7, which is due to repulsion from the xenon free electron pairs (*130*). A study of the mean amplitudes of vibrations of the $[XeF_5]^-$ ion has also confirmed that the lone pairs exert repulsion, which forces bond lengthening (*131*).

Complexes of $XeOF_4$ with CsF, RbF, KF, and NOF were first prepared in the 1960s (*12*). The alkali-metal compounds were prepared by treating the fluorides with an excess of $XeOF_4$ and pumping to constant weight under appropriate conditions (for example, see Scheme 2). The structures of the 3 : 1 complexes were shown by X-ray crystallography to contain the $[F(XeOF_4)_3]^-$ anion, which consists of three essentially undistorted $XeOF_4$ units solvating an F^- anion (*132*, *133*). On the basis of vibrational spectroscopic data (*133*), the $[XeOF_5]^-$ anion in $Cs^+[XeOF_5]^-$ was assigned a low-symmetry C_s struc-



SCHEME 2. The reaction of $XeOF_4$ with CsF.

ture. However, recently two independent studies have described reinvestigations of this anion with different cations. Based on vibrational spectroscopic data and *ab initio* calculations, the $[N(CH_3)_4]^+$ salt has been shown to have a pentagonal pyramidal (C_{5v}) structure (*134*), and an X-ray single-crystal structure on the $[NO]^+$ salt also indicates a similar pentagonal pyramidal arrangement for the anion with the oxygen apical and in which xenon is coordinatively unsaturated and forms two weak interactions with adjacent anions (*135*).

A new synthesis of $Cs^+[XeO_2F_3]^-$, by recrystallization from a $CsF/Cs^+[XeOF_5]^-/XeO_2F_2$ mixture, and a preparation of an unstable adduct, $[NO_2]^+[XeO_2F_3\cdot nXeO_2F_2]^-$, from the reaction of XeO_2F_2 with FNO_2, have been reported (*100*). The two oxygen atoms in $[XeO_2F_3]^-$ are *cis* and not *trans* to each other. The Raman spectrum previously attributed to $Cs^+[XeO_2F_3]^-$ has been shown to be due to $Cs^+[XeO_2F_3\cdot nXeF_2]^-$.

c. Fluoride/Anion Metathesis Reactions between Xenon Fluorides and an Anhydrous Acid Reactions involving the replacement of fluorine in xenon fluorides with other groups began with studies of the reactions of XeF_2 with anhydrous oxygen-containing acids (*3*, *4*, *9*, *13*):

$$XeF_2 + HL \rightarrow F\text{–}Xe\text{–}L + HF \tag{16}$$

$$XeF_2 + 2HL \rightarrow L\text{–}Xe\text{–}L + 2HF. \tag{17}$$

In all of the earlier cases the linkage to the xenon was via the electronegative oxygen (L = $OCOCH_3$, $OCOCF_3$, ONO_2, $OPOF_2$, OSO_2F, $OSeF_5$, $OTeF_5$, $OClO_3$, or OIF_4O). Only those containing the highly electronegative pseudo-halogens, $-OSeF_5$ and $-OTeF_5$, are stable under ordinary conditions. The $-OSO_2F$ and $-OIF_4O$ derivatives decompose readily, and the rest are explosive. Recently, reaction of xenon bis(trifluoroacetate) with trifluoromethanesulfonic acid (triflic acid) has given the novel and highly reactive unsymmetrical xenon-oxo species $CF_3COOXeOSO_2CF_3$ (*136*). Most new work in this area, however, has been concerned with species containing the $OTeF_5$ or $OSeF_5$ groups. The high electronegativity of the $OTeF_5$ group means that $Xe(OTeF_5)_2$ is chemically similar to XeF_2, and interesting reactions with a variety of fluoro-olefins and fluorocarbon iodides have provided useful pathways to a variety of substituted fluorocations (*137–139*). More recently, further work in this area has shown that $Xe(OTeF_5)_2$ reacts with an excess of perfluorobutadiene to yield mostly $TeF_5OCF_2CF{=}CFCF_2OTeF_5$ with a small trace of $TeF_5OCF_2CF(OTeF_5)CF{=}CF_2$. These are the first examples of $-OTeF_5$-substituted unsaturated fluorocarbons (*140*). The products of a similar reaction with perfluorocyclohexene were found to be temperature dependent. At 95°C a high yield of $c\text{-}C_6F_{10}(OTeF_5)_2$ was obtained as expected, but at 115°C the main product was the mono $-OTeF_5$-substituted compound $c\text{-}C_6F_{11}OTeF_5$, indicating that, at the higher temperature, fluorination of one of the $C{=}C$ carbons occurs (*140*). Reaction of $Xe(OSeF_5)_2$ with $CF_2{=}CF_2$, $CF_3CF{=}CF_2$, $CF_2{=}CFCl$, and $CF_2{=}CFH$ has shown that the $OSeF_5$ group cannot be added to olefinic double bonds as cleanly as its tellurium analog. As well as modest yield addition of two $OSeF_5$ groups to the double bond, higher yields of $C_2F_5OSeF_5$, $n\text{-}C_3F_7OSeF_5$, and SeF_5OCF_2COCl are also formed. In the case of $c\text{-}C_5F_8$ only monosubstitution occurred (*141*).

The ability of $Xe(OTeF_5)_2$ to introduce two $OTeF_5$ groups oxidatively has previously been exploited in the synthesis of neutral high-oxidation-state $-OTeF_5$ derivatives from an appropriate neutral low-oxidation-state derivative. For example, $Te(OTeF_5)_6$ can be prepared from $Te(OTeF_5)_4$ (*142*), $I(OTeF_5)_5$ from $I(OTeF_5)_3$ (*143*), and $ORe(OTeF_5)_5$ from $ORe(OTeF_5)_4$ (*144*). This same approach has now been used for the synthesis of $-OTeF_5$-substituted anionic species in the form of the weakly coordinated tetraalkylammonium pnicogen anion series, $[M(OTeF_5)_6]^-$ (M = As, Sb, or Bi). The arsenic and bismuth anions were prepared by the reaction of the $M(OTeF_5)_5$ derivative (M = As or Bi) with a small excess of $[N(CH_3)_4]^+[OTeF_5]^-$ in SO_2ClF, but the instability of $Sb(OTeF_5)_5$ made this an inappropriate precursor for $[Sb(OTeF_5)_6]^-$. Consequently, a two-step process in which $[Sb(OTeF_5)_4]^-$ was first prepared and then oxidized to $[Sb(OTeF_5)_6]^-$ with $Xe(OTeF_5)_2$ was used (*145*).

An intriguing extension of the chemistry of xenon(II) pentafluoroorthotellurates has been a study of the ability of the $OTeF_5$ group to participate in nonredox metathetical fluorinations and to be replaced by a suitably strong protonic acid. Thus, it has been shown that dissolution of $[XeOTeF_5]^+[AsF_6]^-$ in BrF_5 results in the formation of the fluorine-bridged cations $[FXeFXeOTeF_5]^+$ and $[XeF_2 \cdot BrOF_2]^+$ (*146*).

The reaction of XeF_2 with bidentate ligands has been regarded as a particularly interesting challenge, and in 1989 it was shown that it reacts with *cis*-$(HO)_2TeF_4$ to form a polymer $(XeO_2TeF_4)_n$ that is stable to around 80°C. The reaction of *cis*-$(HO)_2TeF_4$ with $[Xe_2F_3]^+[AsF_6]^-$ gives a material with the composition $[FXeOTeF_4OXe]^+[AsF_6]^-$. Recrystallization of the latter in anhydrous HF gave the HF-solvolyzed species $HF[HOTeF_4OXe]^+[AsF_6]^-$, for which an X-ray single-crystal structure was obtained. This shows that the complex is closest to approaching a purely ionic formulation of any xenon complex so far isolated. The $Xe{---}F{-}AsF_5$ contact is 245.8 pm compared with 234.0 pm in $[XeF]^+[Sb_2F_{11}]^-$ (*147*).

The use of $B(OTeF_5)$ to prepare $-OTeF_5$ derivatives of many binary fluorides has inevitably impacted on xenon chemistry. In 1978 $Xe(OTeF_5)_4$ was reported (*148*), and in 1979 $Xe(OTeF_5)_6$ was prepared for the first time by the reaction of XeF_6 with $B(OTeF_5)_3$ in perfluoro-*n*-pentane at −40°C and the $XeOF_4$ derivative $XeO(OTeF_5)_4$ was prepared by a similar route, or by hydrolysis of the xenon hexakis{pentafluorooxotellurate(VI)} (*149*). All three were discussed in more detail two years later (*150*). More recently a series of mixed fluoro/pentafluoro-orthotellurate derivatives of $XeOF_4$ and XeO_2F_2 have been prepared. The novel compound $O_2Xe(OTeF_5)_2$ was prepared according to Eq. (18):

$$XeO_2F_2 + 2B(OTeF_5)_3 \rightarrow 3O_2Xe(OTeF_5)_2 + 2BF_3. \qquad (18)$$

With excess of XeO_2F_2, a mixture of $O_2Xe(OTeF_5)_2$, $O_2XeF(OTeF_5)$, and XeO_2F_2 is produced (*151*). The structures of all of these species and of the related $Xe(OSeF_5)_2$ have been of interest since they were first prepared because the ligands are almost completely unable to form bridging in either solid or liquid structures. It has been anticipated, therefore, that xenon derivatives of these ligands will exhibit the expected geometry of the central atom without influence from weaker interactions. The structure of $Xe(OTeF_5)_6$, although based only on X-ray powder data, has been shown to be a true derivative of XeF_6 (*146*). More recently, a single-crystal X-ray study of $Xe(OTeF_5)_4$ has demonstrated that this, too, is as expected, the xenon being surrounded by four equidistant oxygen atoms in a square planar arrangement. The structure of $O_2Xe(OTeF_5)_2$, formed according to the reaction represented by Eq. (18), shows a very distorted tetrahedral or pseudo-trigonal bipyramidal arrangement about the xenon, which is not consistent with VSEPR predictions (*152*).

Stable oxygen-bonded xenon(II) and xenon(IV) derivatives of the highly electronegative $O{=}IF_4O$ group have also been prepared. The generally convenient route to such species by direct interaction of the xenon fluoride with the acid, in this case $HOIOF_4$, was not used because it is unsafe; instead, the IO_2F_3 dimer was used in insertion reactions of the type shown in Eqs. (19) or (20) in SO_2ClF, $CFCl_3$, HF, or BrF_5 solvents, or an acid displacement reaction between $Xe(OTeF_5)_2$ and $HOIOF_4$ in $CFCl_3$ solvent [Eq. (21)] was used:

$$XeF_2 + (IO_2F_3)_2 \rightarrow FXeOIF_4O + IOF_3 + \tfrac{1}{2}O_2 \tag{19}$$

$$FXeOIF_4O + (IO_2F_3)_2 \rightarrow Xe(OIF_4O)_2 + IOF_3 + \tfrac{1}{2}O_2 \tag{20}$$

$$Xe(OTeF_5)_2 + 2HOIOF_4 \rightarrow Xe(OIF_4O)_2 + 2HOTeF_5 \tag{21}$$

In solution, the products of Eqs. (19) and (20) are mixtures of *cis* and *trans* isomers, but the solid obtained from Eq. (21) is the *cis*, *cis*-$Xe(OIOF_4)_2$ compound (*153*, *154*). The reaction of XeF_4 with IO_2F_3 in a 1:2 ratio in $CFCl_3$ solution produced $F_3XeOIOF_4$ (*153*). Efforts to bring about ammonolysis of XeF_2 and XeF_4 have resulted in the formation of xenon, nitrogen, HF, and ammonium fluoride. Reaction of excess of ammonia and XeF_6 yields the same products, whereas reaction between ammonia and an excess of XeF_6 gives an explosive, white solid (*96*).

The first claim for the successful synthesis of a xenon–nitrogen bond was made in 1974 (*155*). Initial skepticism, based on concerns that the species might actually involve xenon–oxygen rather than xenon–nitrogen bonds, was removed in the early 1980s when the Xe–N-bonded configuration was definitively demonstrated by a single-crystal structure analysis of $FXe[N(SO_2F)_2]$ carried out at 218 K (Fig. 5) (*156*).

In the meantime, a second Xe–N-bonded species had been proposed with the formulation $[\{(FSO_2)_2NXe\}_2F]^+[AsF_6]^-$ (*157*), and another paper, which outlined further details of these two species and a new compound $Xe[N(SO_2F)_2]_2$, was published (*158*). The species $FXe[N(SO_2F_2)_2]$ and $Xe[N(SO_2F)_2]_2$ were prepared by the low-temperature reactions of XeF_2 with $HN(SO_2F)_2$ whereas the complex salt $[\{(FSO_2)_2NXe\}_2F]^+[AsF_6]^-$ was prepared by reaction of $FXe[N(SO_2F)_2]$ with AsF_5 (*158*). The compounds were characterized by multinuclear NMR spectroscopy (^{19}F and ^{129}Xe) (*158*), and the nature of $Xe[N(SO_2F)_2]_2$ was

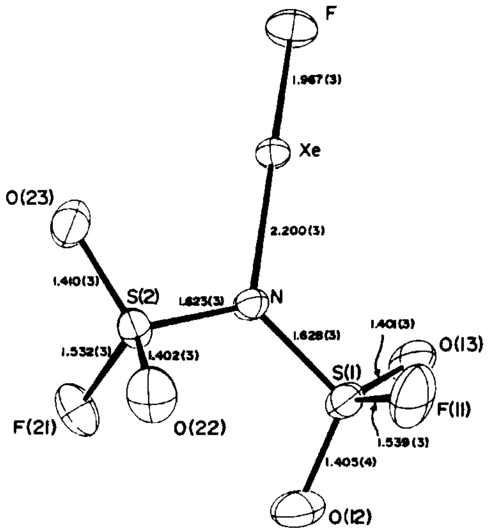


FIG. 5. Perspective drawing of $FXeN(SO_2F)$ showing bond lengths. [Reprinted with permission from (*156*); copyright 1982 the American Chemical Society.]

subsequently confirmed by multinuclear magnetic resonance spectroscopy of the ^{15}N-enriched compound (*159*).

More recently, the fluoride-ion-donor properties of $FXe[N(SO_2F)_2]$ have been exploited in the synthesis of adducts with stoichiometries, $FXe[N(SO_2F)_2]\cdot AsF_5$, $FXe[N(SO_2F)_2]\cdot 3SbF_5$, and $2\{FXe[N(SO_2F)_2]\}\cdot AsF_5$ (*160*). All of the compounds were enriched to 30% with ^{15}N and studied by multinuclear magnetic resonance (^{15}N, ^{19}F, ^{129}Xe) and Raman spectroscopy, which has shown that the adducts can best be described in terms of predominantly ionic formulations, $[XeN(SO_2F)_2]^+[AsF_6]^-$, $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$, and $[F\{XeN(SO_2F)_2\}]^+[AsF_6]^-$. The crystal structure of the $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$ was determined from three-dimensional X-ray data at −64°C and contains discrete $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$ species (Fig. 6) in which the cation is Xe–N-bonded. The Xe–N bond length [2.02(1) Å] is somewhat shorter than that in $FXe[N(SO_2F)_2]$[2.00(3) Å], and the cation and anion are linked by a weak covalent *cis*-fluorine bridge bond in which the Xe---F bond length is 2.457(8) Å (*160*).

Xenon–nitrogen chemistry has been further extended and a new class of Xe–N bonded compounds obtained by the reaction of Lewis acidic $[XeF]^+$ with the lone pair of a series of nitriles. The first of this new series were obtained by the reaction of the appropriate nitriles $RC{\equiv}N$ ($R = H, CH_3, CH_2F, C_2H_5, C_2F_5, C_3F_7, C_6F_5$) with either $[XeF]^+$

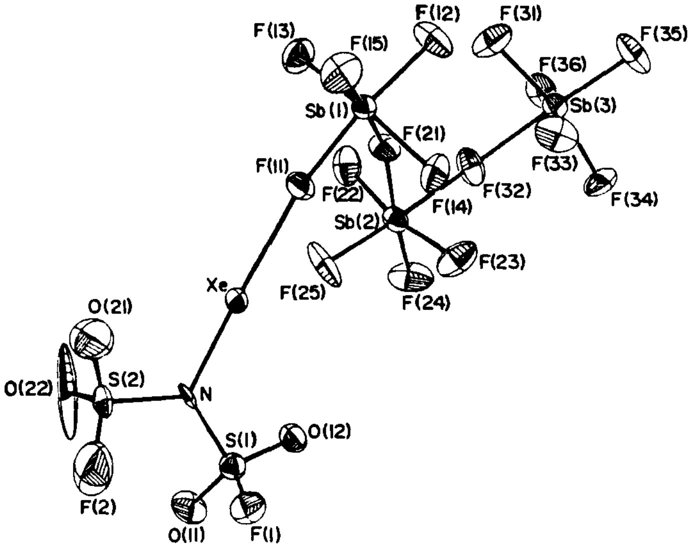


FIG. 6. Perspective drawing of the $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$ structural unit. [Reprinted with permission from *(160)*; copyright 1986 the American Chemical Society.]

$[AsF_6]^-$ or $[Xe_2F_3]^+[AsF_6]^-$ in anhydrous HF at low temperature *(161)*. Subsequently, other novel xenon–nitrogen-bonded cations have been observed by the reaction of $R_FC{\equiv}N$ (R_F = CF_3, C_2F_5, n-C_3F_7) in a similar way *(35)* and by the reaction of equimolar quantitites of $[XeF]^+[AsF_6]^-$ with the perfluoropyridines, 4-RC_5F_4N (R = F or CF_3) in anhydrous HF at −30 to −20°C or at −30°C in BrF_5 solutions *(162)*. The cations, $[C_5F_5N{-}XeF]^+$ and $[4\text{-}CF_3C_5F_4N{-}XeF]^+$, are stable at −30°C and can be isolated from BrF_5 solution as the $[AsF_6]^-$ salts. Low-temperature Raman and multinuclear magnetic resonance (^{14}N, ^{19}F, ^{129}Xe) studies suggest that the cations are planar, with the xenon atom coordinated to the aromatic ring through the nitrogen lone pair (Fig. 7).

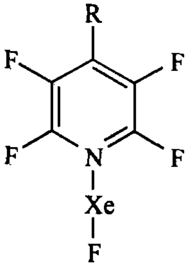


FIG. 7

These nitrogen bases are all oxidatively resistant and have first adiabatic ionization potentials close to the electron affinities of $[Xe-F]^+$ [see reference (*35*) and Section IV]. The estimated electron affinity of $[XeF]^+$ is 10.9 eV and the first ionization potential of *s*-trifluorotriazine, *s*-$C_3F_3N_3$, is 11.50 eV, which led to the idea that the [*s*-$C_3F_3N_2N-XeF]^+$ cation should exist. Reaction of the liquid triazine with $[XeF]^+[AsF_6]^-$ at room temperature, followed by removal of excess of the *s*-trifluorotriazine under vacuum, left a white powder that is stable indefinitely at room temperature, for which multinuclear magnetic resonance (^{19}F, ^{129}Xe) and Raman spectroscopic studies indicate clearly that it is the Xe–N-bonded cation [*s*-$C_3F_3N_2N\text{-}XeF]^+$ (Fig. 8) (*35*).

The most recent attempt to extend xenon–nitrogen chemistry has been an investigation of the reactions of XeF_2 with HN_3, NaN_3, and NaOCN in solution in H_2O, anhydrous HF, or SO_2ClF. Although no stable xenon–nitrogen compounds were obtained, on the basis of product distribution, $FXe(N_3)$ and FXe(NCO) have been postulated as intermediates and *ab initio* calculations have shown that both possess stable minima (*163*).

Since noble-gas chemistry was initiated in 1962, there has been interest in the possibility of making a xenon–carbon bond. Experiments in 1979 appeared to have provided a solution. When xenon difluoride was bled into the tail of a trifluoromethyl radical plasma, a volatile, waxy white solid was produced and trapped at −196°C. The reported properties of this material are consistent with the formulation, $Xe(CF_3)_2$ (*164*), but until this is independently confirmed, some doubt remains about its authenticity.

In 1989, two groups working independently prepared pentafluorophenylxenon borates by nucleophilic displacement of fluorine in XeF_2 using $B(C_6F_5)_3$ as an aryl-transfer reagent. The resulting colorless solid, which has a stable xenon–carbon bond, was characterized in solution by ^{129}Xe and ^{19}F NMR [e.g., Eq. (22)] (*165*, *166*):

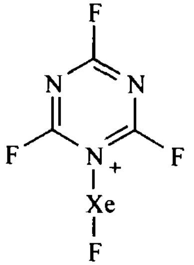


FIG. 8

$$XeF_2 + B(C_6F_5)_3 \xrightarrow{\text{MeCN}} [C_6F_5Xe]^+[B(C_6F_5)_3F]^- + BF_3 \cdot MeCN + BF_4^-. \qquad (22)$$

Reactions with $Te(C_6F_5)_2$ and C_6F_5I yielded $[(C_6F_5)_3Te]^+$ and $[(C_6F_5)_2I]^+$ respectively (*165*), and the hydrolysis and thermal stability of $[C_6F_5Xe]^+$ were also reported (*166*). Very soon afterward more spectroscopic information was provided, and the Xe–C bond length was obtained in an X-ray structural determination on $[MeCN{\cdots}Xe{-}C_6F_5]^+[(C_6F_5)_2BF_2]^-$ (Fig. 9) (*167*).

Since then, several arylxenon derivatives have been prepared via exchange reactions of XeF_2 and triarylboranes. The salts vary in thermal stability; the 2,6-difluoroaryl species are more stable than the monofluoroaryl derivatves, and the parachlorophenyl derivative decomposes at about 0°C (*168*). Reactions of arylxenon species, and especially $[C_6F_5Xe]^+$, have become an area of intense activity. With PhX, $[C_6F_5Xe]^+[AsF_6]^-$ reacts to give isomeric mixtures of biphenyls, $XC_6H_4C_6F_5$ (X = Me, F, CF_3, NO_2, CN) (*169*). Reaction of the same salt with cesium pentafluorobenzoate in water [Eq. (23)] gives an unexpectedly stable covalent acyloxyxenon(II) derivative, the X-ray crystal structure of which indicates a linear $F_5C_6{-}Xe{-}O$ arrangement with dimerization through oxygen bridging (*170*):

$$[C_6F_5Xe]^+[AsF_6]^- + Cs[O_2CC_6F_5] \rightarrow C_6F_5XeO_2CC_6F_5. \qquad (23)$$

The first alkenylxenon(II) derivative has been obtained by the reaction of $[C_6F_5Xe]^+[AsF_6]^-$ with xenon difluoride in anhydrous HF, the reaction proceeding in two steps giving first the (heptafluoro-1,4-cyclo-

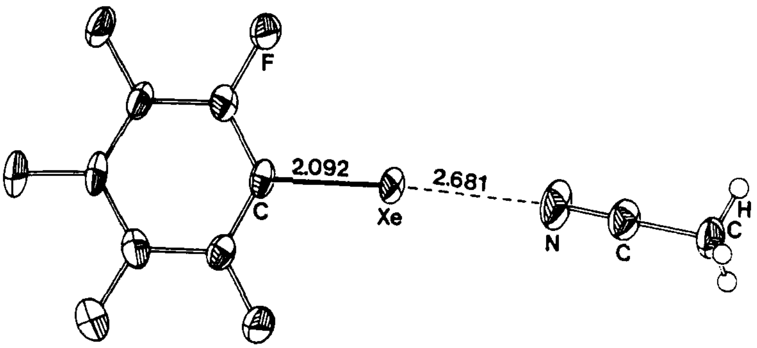
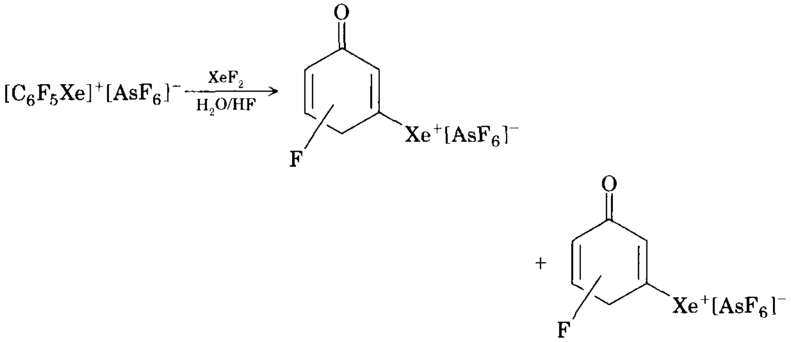


FIG. 9. The structure of the $[MeCN{-}Xe{-}C_6F_5]^+$ cation showing the Xe–ligand bond distances. [Reprinted with permission from (*167*); copyright 1989 VCH Verlagsgesellschaft mbH.]

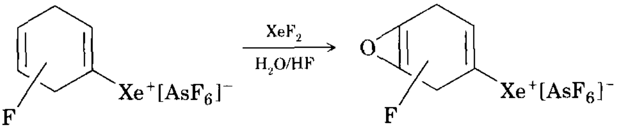
hexadien-1-yl)xenon(II) derivative and then the (nonafluorocyclohexene-1-yl)xenon(II) salt (*171*):

$$[C_6F_5Xe]^+ \rightarrow [C_6F_7Xe]^+ \rightarrow [C_6F_9Xe]^+. \qquad (24)$$

Reactions of $[C_6F_5Xe]^+[AsF_6]^-$ (i) with halide ions in acetonitrile to give aromatic and coupled aromatic molecules (*172*) and (ii) with pyridines of different basicities, where coordination weakens the Xe–C bond and promotes C_6F_5 radical formation, have been described (*173*). As part of this work the adduct $[Xe(C_6F_5)(NC_5H_3F_2\text{-}2,6)]^+[AsF_6]^-$ has been prepared and characterized crystallographically (*173*). Xenon difluoride in aqueous HF acts as a strong electrophilic oxygenation system, and reaction of both $[C_6F_5Xe]^+[AsF_6]^-$ and $[C_6F_7Xe]^+[AsF_6]^-$ with this system has yielded new examples of the transformation of an organic moiety bonded to xenon without cleavage of the Xe–C bond (*174*):



(25)



(26)

Reactions of $[C_6F_9Xe]^+[AsF_6]^-$ with halide ions have been shown to be solvent dependent. With iodide and bromide, in both acetonitrile and anhydrous HF, the xenon is displaced by the halide to give C_6F_9X(X = Br or I). Chloride and fluoride do not react in anhydrous HF, but in acetonitrile the fluoride ions initiate the formation of alkenyl radicals, which abstract hydrogen from the solvent to give C_6F_9H, whereas chloride shows intermediate behavior, giving both C_6F_9H and C_6F_9Cl (*175*). The structure of $[(C_6H_3F_2\text{-}2,6)Xe]^+[BF_4]^-$ in the solid state is an ion pair with an Xe---F distance of 279.3 pm. This is about 70 pm shorter than the van der Waals distance (*176*). Anion exchange of this salt with trimethylsilyltriflate gives the related triflate salt as expected (*177*).

Perhaps the most exciting chemistry to emerge so far from investigation of arylxenon derivatives is a preliminary report of the reaction of $[C_6F_5Xe]^+$ with chloride ions in acetonitrile at below −30°C, which has led to the synthesis and structural characterization of $[(C_6F_5Xe)_2Cl]^+[AsF_6]^-$ and the NMR spectroscopic identification of the more thermally labile compound C_6F_5XeCl, both containing Xe–Cl bonds (*178*). Other interesting chemistry includes electrophilic substitution of fluorobenzenes or trifluoromethylbenzenes using the unsymmetrical xenon–oxo species mentioned earlier (*136*) to give the arylxenon trifluoromethylsulfonates as colorless solids (*179*). Subsequently, $CF_3COOXeOSO_2CF_3$ has been used in a variety of reactions with a range of benzene derivatives containing electron-withdrawing groups such as $-F$, $-CF_3$, $-Cl$, and $-NO_2$ to yield a number of arylxenon trifluoromethylsulfonates. These have been characterized mainly by NMR, mass, and vibrational spectroscopy; however, the structure of $[Xe(2,6\text{-}F_2C_6H_3)]^+[OSO_2CF_3]^-$ has been determined by single-crystal X-ray diffraction methods, which have shown that the arylxenon is weakly coordinated by one oxygen atom of the anion (*180*).

In a related area, interest in the isolation of alkynyl iodonium salts has led to the synthesis of analogous isoelectronic xenon(II) derivatives. These have been obtained by reaction of XeF_2 with $Bu^tC{\equiv}CLi$ or $RC{\equiv}CSiMe_3$ in $BF_3 \cdot OEt_2$ (*181*):

$$R{-}C{\equiv}C{-}SiMe_3 + BF_3 \cdot OEt_2 + XeF_2 \rightarrow [R{-}C{\equiv}C{-}Xe]^+[BF_4]^- + Me_3SiF. \quad (27)$$

As well as chemical reactions, some physical measurements have been made. In particular, cyclic voltametric measurements have yielded reduction potentials for a series of arylxenon(II) tetrafluoroborate salts that indicate that these are stronger oxidizers than the comparable aryliodonium salts (*182*).

3. *Reactions in Which the Xenon Fluoride Acts as a Fluorinating Agent*

As outlined in Section IV, p. 55, the xenon fluorides and their cationic derivatives are capable of oxidation and/or fluorination of many other species. The oxidizing/fluorinating strength is in the sequence, $XeF_2 \approx$ covalent Xe(II) derivatives $< XeF_4 < XeF_6$, and their cations are even stronger than the neutral species. It is also known that, in the case of XeF_2, the addition of anhydrous HF enhances its fluorinating ability, and the mechanism has been discussed. Before 1977 there was already a vast literature on the fluorination of organic fluorides, especially using XeF_2, and this topic will not be covered here. However, a comprehensive and authoritative review up to 1977 [see R. Filler in reference (*5*)] and articles within an excellent recent book (*183*) cover this area well, and the reader is referred to these.

Xenon difluoride and the other xenon fluorides were established as good oxidative fluorinating agents in the early days of noble-gas chemistry (*2–4, 13*). Soluble in water, the difluoride was found to be stable in neutral or acid solution and sufficiently strongly oxidizing to convert chloride to chlorine, chromium(III) to chromium(IV), and bromate, $[BrO_3]^-$, to perbromate, $[BrO_4]^-$ (*13*). In direct combination with other species or in reactions in nonaqueous solution, it reacts with main-group and transition-metal compounds and is incorporated into intercalation compounds. Because of the difficulty and danger associated with the manipulation of XeF_4 and XeF_6, the oxidative fluorination chemistry of these is less closely studied. Work carried out up to and including 1980 has been usefully summarized (*13*), and only chemistry carried out since then is covered here.

a. Reactions with Main-Group Species There has been extensive application of XeF_2 as a reagent in main-group chemistry recently. It has been used to cleave the B–O bonds in $B(OR)_3$ to give FXeOR ($R = SO_2CF_3$ or $SO_2C_4F_9$) and $Xe(OR)_2$ ($R = COCF_3$ or COC_2F_5) (*184*). Aryl trimethylsilanes are readily fluorodesilylated with XeF_2 in hexafluorobenzene at room temperature to give aryl fluorides, the reaction occurring via a radical mechanism (*185*), and vinyl stannanes are fluorinated to fluoroalkenes with XeF_2 and silver hexafluorophosphate or trifluoromethanesulfonate, the latter giving the faster conversion (*186*). The silicon and germanium compounds $C_6F_5MX_3$ (M = Si, Ge; X = Cl, Br) undergo halogen exchange with XeF_2 without C–M cleavage. However, if X is fluorine or alkyl, XeF_2 in the presence of $BF_3 \cdot OEt_2$ or with $[XeF]^+[NbF_6]^-$ yields the heptafluorocyclohexadienyl derivative $C_6F_7MX_3$ by the addition of two fluorine atoms to the pentafluorophenyl ring (*187*). The surface chemistry of silicon has also been studied by exposing it to XeF_2 vapor and examining the chemisorption of silicon at room temperature and −150°C using XPS and AES (*188*).

Studies on reactions of main group alkyl and aryl derivatives have been going on for some years. Recent studies have shown that reaction of XeF_2 with $MePh_2P$ and $MePh_2As$ in CH_3CN produces $MePh_2PF_2$ and $MePh_2AsF_2$ respectively, and with 2-$MeC_6H_4P(NEt_2)_2$, 2-$MeC_6H_4PF_2(NEt_2)_2$ is obtained (*189*). Related reactions of XeF_2 with Me_3X (X = N, P, As, or Sb) all proceed smoothly, the rate reflecting the basicity of the substrate, Me_3X. Where X is P, As, or Sb, the difluoride Me_3XF_2 is formed. Where X is N, cleavage of a C–H bond is the main reaction (*190*). Xenon difluoride also oxidizes phosphorus(III) acid derivatives to give either the phosphorus(V) monomer or the ionic salt respectively (*191*),

$$(CF_3CH_2O)_3P + XeF_2 \rightarrow (CF_3CH_2O)_3PF_2 + [(CF_3CH_2O)_4P]^+[PF_6]^- \quad (28)$$

$$(EtO)_2PF \rightarrow (EtO)_2PF_3 \rightarrow [(EtO)_4P]^+[PF_6]^-, \quad (29)$$

and $M(C_2F_5)_3$ (M = As, Sb) (*192*) and (2,6-$F_2C_6H_3)_3Bi$ (*193*) to the difluorides $M(C_2F_5)_3F_2$ (M = As, Sb) and (2,6-$F_2C_6H_3)_3BiF_2$ respectively.

Although protonation of HOF by reaction of AsF_5 or SbF_5 with water and HF was not successful, the fluorination of water with $[XeF]^+[MF_6]^-$ (M = As, Sb) produced pale reddish $[H_2OF]^+[MF_6]^-$ salts almost quantitatively. These can be stored for about 2 h at room temperature without decomposition, but under vacuum release HOF, HF, and MF_5 (*194*).

A wide variety of reactions of XeF_2 and $[XeF]^+$ with low-valent sulfur species have been studied. Thus, an electrophilic fluorination reagent capable of fluorinating carbanions in moderate yield has been observed in the reaction of XeF_2 with sulfur(II) derivatives such as Me_2S (*195*). Reactions of Me_2S (and Me_2O) with XeF_2 in trichlorofluoromethane result in cleavage of C–H bonds to form CH_2F derivatives as the main reaction pathway. In the absence of a C–H bond, for example if neat $(CF_3)_2S$ is used, oxidation to $(CF_3)_2SF_2$ occurs (*190*). The reaction of Me_2S with XeF_2 in nonacidic medium gives rise to a product that is best formulated as $[Me_2SCH_2SMe]^+[F(HF)_n]^-$. In HF solution at −23°C, however, the product is $[Me_2SF]^+$ (*196*). A similar reaction has also been observed in the combination of $(C_6F_5)_2S$ with $[XeF]^+[MF_6]^-$ (M = As, Sb) in HF, which yields deep violet crystals of $[(C_6F_5)_2SF]^+[MF_6]^-$. An X-ray crystal structure determination of the antimony derivative has shown that the cations and anions are connected via interionic fluorine bridges to produce an infinite chain. Another feature is a short S–F bond distance [158.4(3) pm] (*197*). The conversion of CH_3S- to CH_2FS- in methionine and methionylglycine derivatives has also been achieved using XeF_2 in solution in MeCN at or below room temperature (*198*). Oxidation of MeSCN or $S(CN)_2$ to $[Me(NC)SF]^+$ and $[(NC)_2SF]^+$ respectively using $[XeF]^+[MF_6]^-$ (M = As, Sb) has also been reported (*199*). The oxidative fluorination of $(CF_3)_2C{=}NSNCO$ by XeF_2 gives rise to two isomeric sulfur(IV) compounds, $(CF_3)_2CF{-}N{=}S(F)NCO$ and $(CF_3)_2CFN{=}S{=}NC(O)F$. The third possible isomeric product of 1,3 addition, $(CF_3)_2C{=}N{-}S(F){=}NC(O)F$, was not observed (*200*).

The oxidative fluorination of sulfur(IV) compounds such as diphenyl sulfoxide has been shown to occur under mild conditions with XeF_2 and catalytic amounts of chloride ion. In the Ph_2SO case the product is $Ph_2S(O)F_2$, which is formed in essentially quantitative yield within a few minutes. The chloride ion reacts with XeF_2 to produce fluoride ion, and a mechanism is proposed that involves fluorosulfur(IV) anions and fluorosulfur(V) radicals (*201*).

Reactions of Me_2Se with XeF_2 in trichlorofluoromethane proceed smoothly to give Me_2SeF_2 (*190*). Oxidative coupling of R_2Se_2 (R = Ph, biphenyl, alkyl) to unsymmetrical disubstituted acetylenes and cycloalkynes using xenon difluoride has been shown to yield the vicinal (*E*)-fluoroalkenyl selenides in high yield. Alternatively, the PhSeF equivalent can be formed from $PhSeSiMe_3$ and XeF_2 (*202*). Although PhSeCl and PhSeBr are commercially available sources of selenic electrophiles, PhSeF, which is too labile to be isolated, can be generated *in situ* from PhSeSePh with XeF_2 (*203*). This has been used to generate the novel phosphaalkenes from phosphaacetylenes. Reaction of XeF_2 with Ph_2Te gives Ph_2TeF_2 (*189*). In related studies $PhTeF_3$ or PhTeTePh gave $PhTeF_5$, Ph_2TeF_2 or Ph_3TeF_3 gave Ph_2TeF_4, Ph_3TeF or Ph_3TeCl gave Ph_3TeF_3 (with small amounts of Ph_3TeF_2Cl in the case of Ph_3TeCl), and Ph_4Te gave Ph_4TeF_2 (*204*). The latter has subsequently been characterized (*205*). In a study on the synthesis of tetrakis(perfluoroalkyl) tellurium species, $Te(R_f)_4$, the compound $Te(CF_3)_4$ was obtained from the reaction of $Te(CF_3)_2Cl_2$ with $Cd(CF_3)_2$. Reaction of this compound with fluoride ion acceptors gives rise to the complex cation $[Te(CF_3)_3]^+$, and with certain fluorides the complex anion $[Te(CF_3)_4F]^-$ is formed. However, with XeF_2 it appears to be oxidized to $(CF_3)_4TeF_2$ (*206*). The related compound R_4TeF_2 (R = CH_3) was prepared similarly by the reaction of TeR_4 with XeF_2 (*207*). As part of a study of the Lewis acid behavior of $[Te(OTeF_5)_4]$ toward $[OTeF_5]^-$, higher concentrations of the $[FTe(OTeF_5)_4]^-$ anion in solution in

SO_2ClF were generated by the interaction of XeF_2 with $[N(CH_3)_4]^+$ $[Te(OTeF_5)_5]^-$ at −50°C according to Eq. (30) (*51*):

$$2[Te(OTeF_5)_5]^- + XeF_2 \xrightarrow[-50^\circ C]{SO_2ClF} 2[FTe(OTeF_5)_4]^- + Xe(OTeF_5)_2. \quad (30)$$

Liquid bromine reacts with $[XeF]^+[MF_6]^-$ (M = As, Sb) at room temperature in a complex reaction sequence that gives $Br_5^+[MF_6]^-$,

$$3[XeF]^+[MF_6]^- + 8Br_2 \xrightarrow{r.t.} 3Br_5^+[MF_6]^- + 3Xe + BrF_3, \quad (31)$$

and its crystal structure has been determined (*208*).

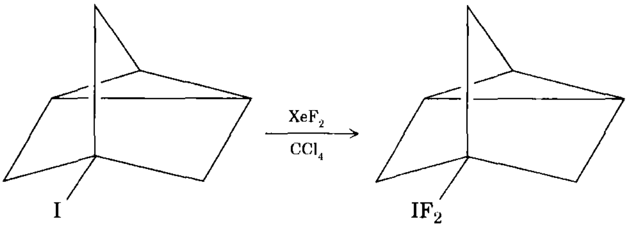
The reaction between HI and $[XeF]^+[AsF_6]^-$ has been shown to give Xe, HF, and $[I_4]^{2+}[AsF_6]_2^-$ as the final products of reaction. No experimental evidence for $[XeI]^+$ was found in the reaction products, and theoretical calculations show that such a species is bound only in the $^1\Sigma$ singlet state and, after interconversion into the unbound triplet state, would immediately dissociate into xenon (^1S) and $I^+(3P)$ (*209*). In synthetic and structural studies of a number of anions the $[IF_2]^-$, $[BrF_2]^-$, and $[IF_4]^-$ salts were synthesized according to Eqs. (32) to (34) (*210*):

$$2[(C_2H_5)_4N]^+F^- + I_2 + XeF_2 \longrightarrow 2[(C_2H_5)_4N]^+[IF_2]^- + Xe \quad (32)$$

$$\begin{tikzcd} CsBr + XeF_2 \arrow[r] & Cs^+[BrF_2]^- + Xe \arrow[d, "{[(C_2H_5)_4N]^+F^-}"] \\ & CsF + [(C_2H_5)_4N]^+[BrF_2]^- \quad (33) \end{tikzcd}$$

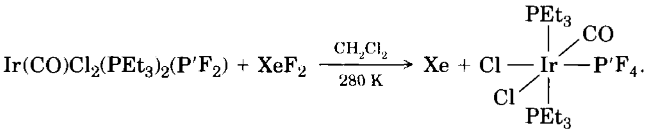
$$2[(C_2H_5)_4N]^+F^- + I_2 + XeF_2 \longrightarrow 2[(C_2H_5)_4N]^+[IF_4]^- + 3Xe. \quad (34)$$

The chemistry of the interaction of XeF_2 with alkyl and aryl iodides has been further extended by investigations of the reactions with CF_3CH_2I, 3,5-$Cl_2C_6H_3I$, and 2-$CF_3C_6H_4I$. In each case the alkyl(aryl) iodine difluoride was obtained (*189*). In related reactions between MeX (X = Cl, Br, or I) and XeF_2, the reactions proceed smoothly, the rate of reaction reflecting the basicity of the substrate, and in the case of MeI, $MeIF_2$ is formed. With MeCl and MeBr, however, MeF is the product (*190*). Although difluoroiodo compounds have been used as synthetic intermediates, none had been isolated until treatment of 4-iodotricyclene with excess of XeF_2 in CCl_4 produced the difluoro derivative [Eq. (35)] as a pale yellow, waxy solid. This is stable in air for a few hours and indefinitely in solution under an inert atmosphere (*211*):



(35)

b. Reactions with Transition-Metal, Lanthanide, and Actinide Species The reaction of chromyl fluoride with XeF_2 at temperatures up to 278°C is a high-yield route to $CrOF_3$ that is superior to other routes (*52*). Reaction with CoF_2, $CoCl_2$, or metallic cobalt have all been shown to yield CoF_3, and DTA data have provided information on the temperatures of initiation of the reactions established (*46*). The mild fluorinating ability of XeF_2 in solution has been exploited in the synthesis of $Ir(CO)Cl_2(PEt_3)_2(P'F_4)$, whose ^{19}F and ^{31}P NMR spectra clearly showed the presence of the $Ir\text{-}P'F_4$ group (*212*):



$$\mathrm{Ir(CO)Cl_2(PEt_3)_2(P'F_2)} + \mathrm{XeF_2} \xrightarrow[280\,\mathrm{K}]{\mathrm{CH_2Cl_2}} \mathrm{Xe} + \mathrm{Cl}-\overset{\mathrm{PEt_3},\ \mathrm{CO}}{\underset{\mathrm{Cl},\ \mathrm{PEt_3}}{\mathrm{Ir}}}-\mathrm{P'F_4}. \qquad (36)$$

It was also found to fluorinate the five-coordinate carbonyl complex of Ir(I), $[Ir(CO)_3(PEt_3)_2]^+$, to yield the first fluoroacyl derivative, $Ir(CO)_2F(COF)(PEt_3)_2$ (*213*). Xenon difluoride also reacts with $[Pt(NH_3)_4]Cl_2$ in the solid state to give *trans*-$[Pt(NH_3)_4F_2]Cl_2$, but in solution in MeCN this is converted to *trans*-$[Pt(NH_3)_4Cl_2]F_2$ (*214*). The analogous oxidation of $[Pt(py)_4]^{2+}[BF_4]_2^+$ gives the crystallographically characterized $[PtF_2(py)_4]^{2+}[BF_4]_2^-$ (*215*).

It was established in the 1970s that XeF_2 in solution was a valuable means of introducing fluorine oxidatively into transition carbonyl compounds to produce carbonyl fluorides (*216*, *217*). Recently, there has been renewed activity in this area, supported by the improvements in multinuclear Fourier-Transform NMR techniques. Among the more recent papers is a report of a reaction of XeF_2 with $[Re_2(CO)_{10}]$ in perfluoro-1,3-dimethylcyclohexane that concludes that the product is $Re(CO)_3F_2$ (*218*) even though the properties of the compound produced are clearly those of $Re(CO)_5F \cdot ReF_5$ (*217*). Considerable progress has been made with oxidative fluorination of ruthenium and osmium carbonyls and their derivatives. Thus, $[Ru_3(CO)_{12}]$ with XeF_2 in anhydrous HF gave, in solution, *cis*-$[RuF_2(CO)_4]$ as the main product along with small amounts of $[RuF(CO)_5]^+$, $[Ru_2F_4(CO)_7]$, $[\{RuF(CO)_4\}_4(\mu\text{-F})]^+$, *mer*- and *fac*-$[RuF_3(CO)_3]^-$, $[\{RuF_2(CO)_3\}_n]$, and $[\{RuF_2(CO)_3\}(\mu\text{-F})\{Ru(CO)_5\}]^+$, all of which have been characterized by ^{13}C, ^{19}F and $^{13}C\text{-}\{^{19}F\}$ NMR spectroscopies. Removal of the HF solvent yielded tetrameric $[\{RuF_2(CO)_3\}_4]$ (*219*). Similarly, the equivalent reaction with $[Os_3(CO)_{12}]$ produced, in solution, a range of mono- and dinuclear osmium carbonyl fluoride species, with *cis*-$[Os(CO)_4F_2]$ as the major product and $[Os(CO)_5F]^+$, $[Os_2(CO)_7F_4]$, and $[Os_2(CO)_8F_3]^+$ as minor products. The main product is stable in solution, but removal of the solvent results in CO loss to give the fluoride-bridged tetrameric analog to the ruthenium tricarbonyl difluoride, $[\{Os(CO)_3F_2\}]_4$ (*220*).

The mechanism of the oxidation of low-valent ruthenium and osmium complexes has also been elucidated by a study of the reaction of XeF_2 with $[M(CO)_3(PPh_3)_2]$ (M = Ru, Os) in dichloromethane (*221*). Fluoroacyl complexes of ruthenium and osmium, $[M(COF)(CO)_2F(PPh_3)_2]$ (M = Ru, Os) were identified as intermediates in the oxidative addition of XeF_2 in solution, and the mechanism, probed by addition of BF_3, has been shown to involve oxidation of the metal center by $[XeF]^+$ to give a monofluorinated cation. Subsequent nucleophilic attack by F^- at the coordinated CO with CO elimination gives, finally, [*OC*-6-13]$[M(CO)_2F_2(PPh_3)_2]$. In the ruthenium case, the ligand arrangement has been confirmed by a single-crystal X-ray crystallographic study (*221*).

Controlled sequential reaction of $[Ir_4(CO)_{12}]$ with XeF_2 in anhydrous HF at low temperature yielded, initially, *fac*- and *mer*-$[Ir(CO)_3F_3]$, and, ultimately, IrF_5. Removal of the solvent at the initial stage of the reaction results in the precipitation of *fac*-$[Ir(CO)_3F_3]$, which contains predominantly σ-bonded carbonyl ligands with high CO-stretching frequencies (*222*).

Xenon difluoride has been shown to react with organomercury compounds, R_2Hg (R = $PhC{\equiv}C$, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$, *p*-$EtO_2CC_6H_4$, and $PhCH_2$), with cleavage of the C–Hg bond to give RHgF or RHgF/HgF_2 mixtures. When R = benzyl, the RHgF formed undergoes fast demercurization. From the composition of the reaction mixtures it has been established that the reactions involve free radicals. The absence of fluorinated organomercury products is evidence that XeF_2 reacts more readily with the C–Hg bond than with C–H or C–C bonds. With HgX_2 (X = Cl, Br, I) under mild conditions, HgF_2, halogen gas, and xenon are produced (*223*).

The xenon fluorides, XeF_2, XeF_4, and XeF_6, have all been used in preparations of some lanthanum tetrafluorides, LnF_4 (Ln = Ce, Pr, or Tb) and their heptafluoro complexes, Cs_3LnF_7 (Ln = Ce, Pr, Tb, Dy, or Tm) (*224*). Detailed examination of the reaction of Cs_3LnCl_6 with XeF_2 at 100–400°C has shown that Cs_3LnF_7 (Ln = Ce, Pr, Tb, Nd, or Dy) species are formed, but for Er and Yb under the same conditions only the lanthanum(III) species Cs_3LnF_6 (Ln = Er or Yb) are produced (*224*).

In the actinide field, stopped-flow spectroscopy has been used to study the oxidation of plutonium(III) to plutonium(IV) in 1*M* $HClO_4$ by XeF_2. Two moles of Pu(III) are oxidized per mole of XeF_2 consumed, and there is no evidence for oxidation to Pu(V) or Pu(VI). Rate constants and activation parameters have been obtained and a mechanism postulated that invokes a sequence of 2 one-electron oxidation steps (*225*). The oxidation of americium by a range of xenon-containing oxidants in $KHCO_3$, $KHCO_3$ and K_2CO_3, and in K_2CO_3 solutions, has been studied (*226, 227*). Xenon difluoride and xenon trioxide convert Am(III) to Am(IV) in solution (*226*), whereas $Na_4[XeO_6]$ oxidizes Am(III) to Am(IV), Am(V), and Am(VI) mixtures unless the perxenate is in excess, when Am(VI) is produced (*226, 227*). The trioxide, XeO_3, reacts with Am(III) only under UV irradiation (*227*).

VI. Radon Chemistry

The chemistry of radon (II) was outlined by Stein in 1983 (*14*). Since then, evidence for radon in a higher oxidation state (RnF_4 or RnF_6) and a radon oxide (RnO_3) has been claimed and disputed, and the ions, $[HRnO_3]^+$, $[HRnO_4]^-$, and $[RnO_3F]$ have been reported.

Soon after the initial discovery of xenon compounds in 1962, a low-volatility fluoride was detected in the product of the combination of radon with fluorine at 400°C (*226*). It was also shown that ^{222}Rn is oxidized by chlorine and bromine fluorides, IF_7 (*227–230*) or $[NiF_6]^{2-}$ (*227–229*) in HF to give stable solutions of radon fluoride, and that radon can be collected as a solid by oxidation of the gas with liquid BrF_3 or the solid complexes $[ClF_2]^+[SbF_6]^-$, $[BrF_2]^+[SbF_6]^-$, $[BrF_4]^+[Sb_2F_{11}]^-$, $[IF_4]^{3+}3[SbF_6]^-$, and $[BrF_2]^+[BiF_6]^-$ (*231–232*). Electromigration studies suggested that in the solution studies the radon is present as $[RnF]^+$ or $[Rn]^{2+}$ (*228, 229*). Such ionic formulations were also favored in relativistic quantum mechanical calculations (*233*). This has been borne out further by more recent chemistry in which solutions of cationic radon have been prepared by oxidation of elemental radon with halogen fluorides and shown to displace hydrogen, sodium, and potassium in solid materials such as Nafion resins (H^+ and K^+ forms), potassium hexafluorophosphate, and sodium hexafluoroantimonate. It has also been shown that radon in this state can be quantitatively recovered by ion exchange and eluted with bromine trifluoride in sulfuryl chloride (*234*). By comparison of the properties of the products from all of these reactions with the known properties of the fluoride and fluoride complexes of krypton and xenon, it is almost certain that radon forms a difluoride, RnF_2, and derivatives such as $[RnF]^+[SbF_6]^-$, $[RnF]^+[TaF_6]^-$, and $[RnF]^+[BiF_6]^-$, which are direct analogs of krypton and xenon species (*235*). This has been further strengthened by the observation of the reaction of radon with solid $[O_2]^+[SbF_6]^-$ at room temperature, which yields gaseous oxygen and an involatile radon compound (*236*). Comparison with xenon chemistry suggests the reaction

$$Rn_{(g)} + 2\{[O_2]^+[SbF_6]^-\}_{(s)} \rightarrow [RnF]^+[Sb_2F_{11}]^-_{(s)} + 2O_{(g)}. \tag{37}$$

This was further substantiated by reactions of radon with fluoronitrogen salts and halogen–fluoride metal salts, and the development of a method of collecting radon from air using $[O_2]^+[SbF_6]^-$ or $[IF_6]^+[SbF_6]^-$ (*237*).

Hydrolysis of radon fluoride with water yields radon, oxygen, and HF. This parallels the reactions of KrF_2 and XeF_2 and is in marked contrast to the reactions of XeF_4 and XeF_6, in which some xenon is retained in solution as Xe(VI). It also coprecipitates with XeF_2 from halogen fluoride solutions and complexes with XeF_2 but not XeF_4 (*238, 239*) all of which points to the fluoride being RnF_2.

Claims by Russian workers that a higher fluoride of radon, RnF_4 or RnF_6, can be prepared in tracer experiments by heating radon, xenon, fluorine, bromine pentafluoride, and either sodium fluoride or nickel fluoride, and converted to RnO_3 by hydrolysis (*240*) appeared to others (*235*) to be due to the precipitation of radon as a solid complex, which is probably $[RnF]_2^+[NiF_6]^{2-}$. However, the precipitation of $CsXeO_3F$ from aqueous solutions results in the coprecipitation of radon, and this has been taken by the Russian group as confirmation that RnO_3 is the product of hydrolysis of the fluoride formed (*241*). Furthermore, it has been suggested that the failure of Stein to observe the high-oxidation-state $[RnO_3F]^-$ species was probably due to high F^- concentration (*242*). More recently, ultracentrifugation of hydrolyzed radon solutions, coprecipitation studies, and kinetic data for the decomposition of the solution species have been interpreted in terms of it being RnO_3 (*243*). Recent electromigration studies have also been used to suggest that in acidic aqueous solutions (pH > 5) cationic, $[HRnO_3]^+$, and anionic, $[HRnO_4]^-$, forms of radon are produced, the validity of the electromigration method having been established using xenon(VI) (*244*).

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