THE COMPOUNDS OF THE NOBLE GASES

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In August of this year, seventy years will have elapsed since the discovery and isolation of the first noble gas, namely argon, by Lord Rayleigh and William Ramsay;[1] but barely two years have passed since the preparation of the first compound of a noble gas.

Even though claims of compound formation by the noble gases have been made since their discovery, the first authentic compound was xenon hexafluoroplatinate(v), $Xe^+PtF_6^-$, reported by Bartlett in June, 1962,[2] as the result of an idea arising from unrelated researches on the synthesis of dioxygenyl hexafluoroplatinate(v), $O_2^+PtF_6^-$.[3,4] It was the similarity of the first ionization potential of molecular oxygen and of atomic xenon at just over 12 eV, that led to Bartlett's forecast.

By today, several of these xenon metal fluorides are known, as well as a succession of other xenon compounds, including fluorides, an oxide and oxyfluorides. In addition, two fluorides of krypton are known and also a radon fluoride.

The remarkable feature about the xenon metal fluorides is that they are formed at room temperature by simple reaction of xenon with the appropriate metal(vi) fluoride, MF_6, according to the equation

$$Xe + MF_6 \rightarrow Xe^+MF_6^- \quad \quad (1)$$
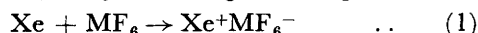
In this way, compounds have been prepared where $M = Pt$,[2] Pu,[5] Ru[5] and Rh.[6] However, the reaction does not proceed with uranium(vi), neptunium(vi) and iridium(vi) fluorides.[5]

Pyrolysis of xenon hexafluoroplatinate(v) gives xenon and a red solid of composition, $Xe(PtF_6)_2$.[6]

Direct reaction between xenon and fluorine at a temperature of 400 °C gives rise to xenon(iv) fluoride,[7] the product being obtained by cooling to -78 °C and pumping off the excess fluorine. Similar conditions have not resulted in the formation of the corresponding krypton compound,[8] although radon(iv) fluoride has probably been obtained in this way.[9] In this last case, assessment of the product has not so far been possible because of the small yields, due to the minute amount of radon available and the inherent radiation hazard arising from the intense radioactivity.

High-temperature flow systems have also been used to prepare xenon(iv) fluoride.[10,11,12]

Both xenon(iv) fluoride[13] and krypton(iv) fluoride[8] are obtained by passage of high-voltage discharges through mixtures of the appropriate gaseous elements at very low temperatures.

Xenon(ii) fluoride has been reported,[7] and identified[5,14,15] as an impurity in xenon(iv) fluoride preparations. The compound is obtained by circulating xenon

and an excess of fluorine through a nickel tube at 400 °C and trapping out the product at -50 °C. In this way, formation of xenon(iv) fluoride by the stage

$$XeF_2 + F_2 \rightarrow XeF_4 \quad .. \quad \quad (2)$$
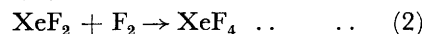
can be checked.[11] Any xenon(iv) fluoride present as impurity can be separated by flushing the vapours from the system.[14]

Ultra-violet photolysis of xenon and fluorine in an all-nickel vessel fitted with sapphire irradiation windows gives xenon(ii) fluoride with only a trace of xenon(iv) fluoride.[16] In addition, ultra-violet irradiation at 20°K of fluorine, xenon and argon mixtures deposited on caesium iodide crystals yields xenon(ii) fluoride.[17] This method, known as the matrix-isolation technique, has also yielded krypton(ii) fluoride from mixtures of fluorine, krypton and argon.[17] Krypton(ii) fluoride has also been obtained by bombarding krypton and a modest excess of fluorine with 1·5 meV electrons at -150 °C.[18]

Returning to xenon(ii) fluoride, this compound has also been obtained as condensate on a cold finger at -78 °C, by passing discharges provided by an induction coil through mixtures of xenon and fluorine.[19,20] However, an important development in the preparation of xenon(ii) fluoride is the dispensation with elemental fluorine in the preparation by high-voltage discharge of a mixture of xenon and carbon tetrafluoride.[21] Successful preparations have been similarly obtained with CF_3OF and FSO_3F.[22]

The only other simple fluoride of the noble gases that has been obtained to date is xenon(vi) fluoride prepared by heating xenon and excess of fluorine to temperatures above 300 °C,[23,24,25,26] very high pressures being also used.[23,24,26]

The three xenon fluorides are colourless solids, the room-temperature vapour pressure of the xenon(ii) and xenon(iv) compounds being about 3 mmHg, while that of the xenon(vi) compound at 20 °C is 27 mmHg.[5,7,11,20,23,25] Melting points range from 46 °C for xenon(vi) fluoride,[23] through 100 °C for xenon(iv) fluoride[7] to between 120 °C[20] and 140 °C[11] for xenon(ii) fluoride.

Crystallographic studies have shown[27-30] that xenon (iv) fluoride crystals are of the monoclinic system of density 4·04 to 4·10 g cm^{-3} with a second, less stable modification[29] having density 4·42 g cm^{-3}. The xenon (ii) fluoride crystal[28] is body-centred tetragonal of density 4·32 g cm^{-3}.

The structures of the xenon fluorides have been compared with the polyhalides, and, by analogy with

halogen fluorides and chlorides, a linear structure based on the trigonal bipyramid sp^3d hybridized arrangement of electron pairs is proposed for xenon(II) fluoride,[31,32,33] while a square planar arrangement, based on the octahedral sp^3d^2 arrangement of electron pairs, is suggested for the xenon(IV) compound.[31,32,33] However, the octahedral geometry of xenon(VI) fluoride cannot be accommodated on models such as these, and an alternative view in which the d orbitals of the noble gas are of little importance, has been promoted.[22,31,34] This proposal, where the bonding has been ascribed to delocalized molecular orbitals formed mainly by a three-centre four-electron combination of p σ-type xenon and fluorine orbitals,[31,35,36,37,38] predicts the correct geometries for all three xenon fluorides. The remote possibility of a tetrahedral xenon(IV) fluoride has not been completely discounted.[7,39]

The linear and square planar configurations for xenon(II) fluoride and xenon(IV) fluoride, respectively, have been confirmed by spectroscopic studies,[5,7,11,40,41,42] including n.m.r. spectroscopy,[43,44,45,46] as well as by X-ray[5,10,27,28] and neutron-diffraction[29,47] investigations.

Infra-red spectra have established a symmetrical structure for xenon(VI) fluoride,[23] but on the basis of an infra-red absorption band at 1225 cm^{-1}, Agron et al.[11] favour covalent bonding based on a xenon valence shell of sp^3d^3 orbitals instead of the octahedral structure.

On the evidence of X-ray crystal-structure investigation,[10,27] and of the more precise method of neutron diffraction,[29] the Xe–F bond length in xenon(IV) fluoride is 1·95Å. The value of 1·85Å obtained for the gas molecule from vibrational spectroscopic studies[42] is in reasonable agreement. Within the limit of experimental uncertainty, the molecule of xenon(IV) fluoride is regarded as square planar with four equal F–Xe–F angles of 90°.[10,27,29]

The accepted Xe–F bond length in the linear xenon(II) fluoride is the neutron diffraction value of 2·00Å.[47] The value obtained for the gaseous molecule (1·7Å) from the infra-red vibrational P–R spacing is much lower.[11,14]

The bond energies of the Xe–F bonds in xenon(II) fluoride,[22,48,49] as well as in xenon(IV) fluoride[48,49,50] and xenon(VI) fluoride,[22] fall around 30 kcal per Xe–F bond. These have been calculated from enthalpies of formation deduced theoretically[22,48] and by experiment.[49,50] Enthalpies of sublimation are available for these fluorides[51] as well as for the xenon(VI) fluoride.[8]

The krypton fluorides are less stable than the corresponding xenon compounds.[8,18] While no data appear to have been published for krypton(IV) fluoride, the krypton(II) compound has been assigned a linear symmetry on infra-red evidence.[17] The parity of the force constants for this, and the xenon(II) compound, indicates that the bond energies for the two compounds cannot be far removed.[17] The only experimental thermal datum available in the literature for the krypton fluorides is the value of 8·84 kcal mole^{-1} for the enthalpy of sublimation of the krypton(IV) compound.[8]

Product stoichiometry has, in many cases, been assessed by reactant consumption ratios, but krypton(IV) fluoride is sufficiently unstable for volumetric assay of the recovered krypton and fluorine to provide a further check on the formula.[8] For the relatively more stable xenon fluorides, product stoichiometry has been confirmed by reduction with hydrogen,

$$\text{XeF}_n + \frac{n}{2}\text{H}_2 \rightarrow \text{Xe} + n\text{HF} \quad .. \quad (3)$$
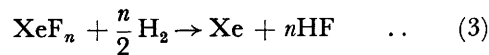
followed by analysis of the products.[7,16,25] Similarly, confirmation can also be obtained by reduction with mercury, giving quantitative xenon release.[13,25] The formulae are also partially verified on the evidence of ion species obtained by mass spectrometry.[5,15,21,23,25]

Xenon(IV) fluoride dissolves in liquid antimony(V) fluoride and in tantalum(V) fluoride to give the respective addition complexes, $\text{XeF}_2,2\text{SbF}_5$ and $\text{XeF}_2,2\text{TaF}_5$.[52]

The iodide ion in aqueous solution liberates xenon, iodine and the fluoride ion from xenon fluorides.[12,20,21,26] The reaction is sometimes complicated by simultaneous hydrolysis.[26,50]

Of the other reactions of the xenon fluorides reported in the literature, the most notable are the hydrolyses, since these give rise to a range of other xenon compounds. Even though the hydrolysis of xenon(IV) fluoride can be represented by the equation

$$\text{XeF}_4 + 2\text{H}_2\text{O} \rightarrow \text{Xe} + 4\text{HF} + \text{O}_2 \quad .. \quad (4)$$
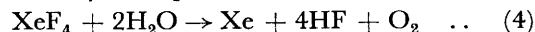
for a wide pH range, the reaction is certainly more complex,[5,7,53,54] and xenon(VI) oxide has been prepared by hydrolysis of xenon(IV) fluoride,[53,54] as has also the species designated, Xe(OH)_4.[55]

Pyrolysis of a mixture of xenon and fluorine containing a fractional percentage of oxygen first provided evidence for the existence of the oxyfluorides, XeOF_3 and/or XeOF_4.[5,15] Other oxyfluorides for which tentative experimental evidence is available include XeO_2F_2,[22,33] XeO_2F_4,[33] XeOF_2[33] and XeO_3F_2.[33]

XeOF_4, a colourless liquid, has also been obtained by the incomplete hydrolysis of xenon(VI) fluoride; complete hydrolysis gives xenon(VI) oxide.[24]

The structure of the xenon oxyfluorides has been explained on the basis of the oxygen atom completing its octet by attachment to a lone pair of electrons on the central xenon atom.[33] In the case of the odd-electron XeOF_3, it is believed that the oxygen atom may be a direct substitution for a fluorine, being satisfied by the partial sharing of a single electron.[39] Infra-red and Raman spectra are in agreement with the square pyramid arrangement for XeOF_4.[24]

Xenon(VI) oxide was first detected by accident in the condensate of xenon(VI) fluoride.[56] The compound is also obtained by the hydrolysis of xenon(VI) fluoride, and of XeOF_4.[24,56]

With the possible exception of krypton(II) fluoride,[18] xenon(VI) oxide is the most unstable compound of the noble gases so far examined.[55] It is particularly explosive and in this respect simulates T.N.T.[57] Its stoichiometry has been confirmed by its reaction with acidified potassium iodide :[54]

$$XeO_3 + 6H^+ + 6I^- \rightarrow 3I_2 + Xe + 3H_2O \quad .. \quad (5)$$
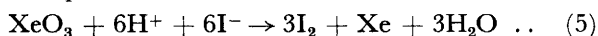
Crystallographic and infra-red spectroscopic data confirm the molecule as having a trigonal bipyramid geometry similar to the isoelectronic iodate ion,[24,54,56] the average $Xe=O$ bond length being $1 \cdot 76 \text{Å}$ and the average $O=Xe=O$ bond angle, $103°$.[54]

Xenic acid, $Xe(OH)_6$, is claimed to be the ionic xenon species resulting from the hydrolysis of xenon(IV) fluoride[5] and xenon(VI) fluoride.[56] The compound, which can be stored at $-30°C$ for several weeks,[58] results from the slow hydrolysis of xenon(VI) fluoride, or xenon oxyfluorides, at $0°C$.[58] Salts of the acid are well established and can be prepared either by the addition of alkali to an aqueous solution of the acid,[58] or by alkaline hydrolysis of xenon fluorides.[59] In the latter case, perxenates are obtained with the octahedral XeO_6^{-4} ion containing Xe^{VIII} species.[59] The silver[22] and sodium[59] salts are known as well as the acid, H_4XeO_6.[22] Acid or neutral hydrolysis of the xenon fluorides gives rise to the xenon(VI) species, XeO_6^{-6}, and the barium, sodium and potassium salts have been prepared.[58]

It is clear that with the characterization of about 20 compounds of this family of elements, the title 'inert' is no longer justified and the term 'noble' has, therefore, been used throughout this brief survey. However, compounds are yet to be prepared for helium, neon and argon, but except for the possibility of ArF_4, these are, at present, considered to be unlikely.[38,48]

In less than two years (June, 1962, to December, 1963), about 60 publications have appeared in this rapidly expanding branch of inorganic chemistry, and while the majority of these have been short communications, the field has been discussed at conference level,[60] and a short review on the subject has also been published.[61]

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