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Chapter 8

NOBLE GASES

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8.1 THE ELEMENTS

The smallest possible doubly charged molecule ion He_2^{2+} has now been detected spectroscopically by charge-stripping mass spectrometry.[1] Although this species is of potential astrophysical interest and of importance in fusion processes it has hitherto only been the subject of quantum mechanical calculations. Stein[2] has shown that radon can be oxidised in CCl_2FCClF_2 or SO_2Cl_2 by BrF_3 or BrF_5: he inferred that radon is in a cationic form since in this state it was quantitatively collected by ion-exchange chromatography and could be eluted with BrF_3 in SO_2Cl_2.

8.2 KRYPTON(II) AND XENON(II)

Reactions of krypton(II) fluoride were reported at the International Symposium on Fluorine Chemistry in Berlin; XeF_6 was found to be a useful solvent for KrF_2 in the preparation of such compounds as $(XeF_5)_2NiF_6$, XeF_5AgF_4, and $(Xe_2F_{11})_2NiF_6$.[3] The reaction of KrF_2 with MO_2, M = Ce, Tb, Pr, in the molar ratio 2:1 or 3:1 generates MF_4;[4] however, using the 1:1 ratio MOF_2 species are formed, which are not just mixtures of MO_2 and MF_4.

$$CeF_3 + \tfrac{1}{2}XeF_2 \rightarrow \tfrac{1}{2}Xe + CeF_4 \qquad ...(1)$$

Kiselev et al.[5] have described the oxidation of Tm(III) to (IV) by XeF_2: the starting material used was Cs_3TmX_6, X = Cl or F. Cobalt, as the metal or CoX_2, is similarly converted to CoF_3.[6]

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The reactions with CeF_3 or TbF_3 were studied by d.t.a.; the product in both instances was the metal tetrafluoride.[7] The enthalpy of reaction (1), deduced from the d.t.a. data was found to be 111±8 kJ mol^{-1}. Xenon(II) fluoride converts Cs_3LnCl_6 to Cs_3LnF_7 for Ln = Ce, Pr, Nd, Dy at temperatures between 100° and 400°C.[8] Fluorination of the rubidium salts Rb_3MF_6, M = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm or Yb was investigated by d.t.a.[9]

Only with M = Ce or Pr were exothermic reactions detected and the products were found to be Rb_3MF_7: with M = Tb or Dy the products appear to contain M(IV) although the d.t.a. technique did not detect reaction.

Shackelford and co-workers have proposed that the addition reactions to alkenes by XeF_2 and methanol proceeds via the intermediate $F\text{-}Xe\text{-}OCH_3$:[10] the influence of protonic and boron acids on the course of the addition is especially remarkable. Foster and Downs[11] have carried out a survey of the reactions of XeF_2 with methyl derivatives of the p-block elements. Reactions proceed smoothly in most cases, although where necessary $CFCl_3$ can be used as a moderator. The formation of the difluorides was observed in most systems, reaction (2). However for Me_nZ,

$$Me_nM + XeF_2 \rightarrow Me_nMF_2 + Xe \qquad \ldots(2)$$

Z = N, O, or S, C-H bond reaction to form $-CH_2F$ derivatives was predominant: for Z = Cl or Br, C-Z bond cleavage occurred. A series of phenyltellurium(VI) fluorides, Ph_nTeF_{6-n}, has been prepared by the oxidative-fluorination of suitable precursors with XeF_2 in solution in CH_2Cl_2 or MeCN.[12] The reaction of $Xe(OTeF_5)_2$ with the halo-olefins $CF_2{=}CFCl$, $CF_2{=}CCl_2$, and $CF_2{=}CFH$ results in addition of two $OTeF_5$ groups across the double bond.[13] The same reagent effects additions across both double bonds of perfluorobutadiene to form $1,2,3,4\text{-}(TeF_5O)_4C_4F_6$ in 97% yield.

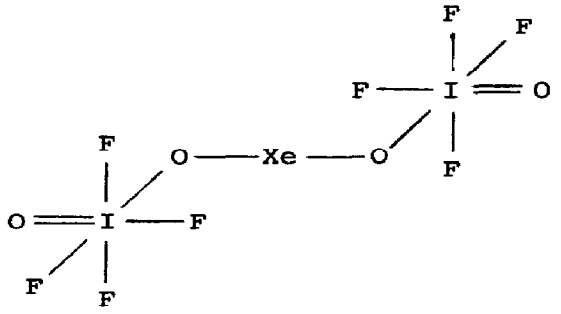
The study of Xe(II) compounds containing the very electronegative group $OI(O)F_4$ continues.[14] An attractive way of avoiding the formation of the shock-sensitive $FOI(O)F_4$ during the synthesis of the Xe(II) compound uses reaction (3) in which the stoichiometric amount of $HOI(O)F_4$ is added and the volatile $HOTeF_5$ is displaced.[14,15] The Raman and n.m.r. (^{19}F and ^{129}Xe) spectra of (1) are consistent with the cis,cis-structure (1). The compound is unstable at room temperature, rapidly undergoing

$$Xe(OTeF_5)_2 + 2HOI(O)F_4 \rightarrow Xe(OI(O)F_4)_2 + 2HOTeF_5 \quad ...(3)$$

$$Xe(OI(O)F_4)_2 \rightarrow \underbrace{IF_5 + IOF_3} + Xe + 1.5O_2 \quad ...(4)$$

$$\downarrow$$

$$\tfrac{1}{2}IF_5 + \tfrac{1}{2}IO_2F$$



(1)

decomposition according to equation (4).

8.3 XENON(IV) AND (VI)

A Xenon(IV) derivative of $HOI(O)F_4$, $F_3XeOI(O)F_4$, has been characterised by ^{129}Xe n.m.r. spectroscopy of a solution of $2XeF_4/IO_2F_3$.[14,15] Kiselev and colleagues[16] have evidence for the reaction between CsF and XeF_4; according to their study the Xe(VI) salt decomposed slowly above 350°C. The corresponding reaction

$$2CsF + 2XeF_4 \rightarrow Cs_2XeF_8 + XeF_2 \quad ...(5)$$

with XeF_2 also gave the same Xe(VI) product but very slowly.

The Cs^+ salts of $XeOF_5^-$ and $[(XeOF_4)_3F]^-$ have been prepared and characterised.[17] The Raman spectra of $Xe^{16}OF_5^-$ and $Xe^{18}OF_5^-$ are consistent with a stereochemically active lone pair on Xe leading to a distorted octahedral arrangement (C_s symmetry). The X-ray structure of $Cs[(XeOF_4)_3F]$ shows the presence of a C_s symmetry anion in which three Xe atoms are attached to F(8), see Figure 1. The use of XeF_6 as a solvent for KrF_2 has been mentioned above.[3]

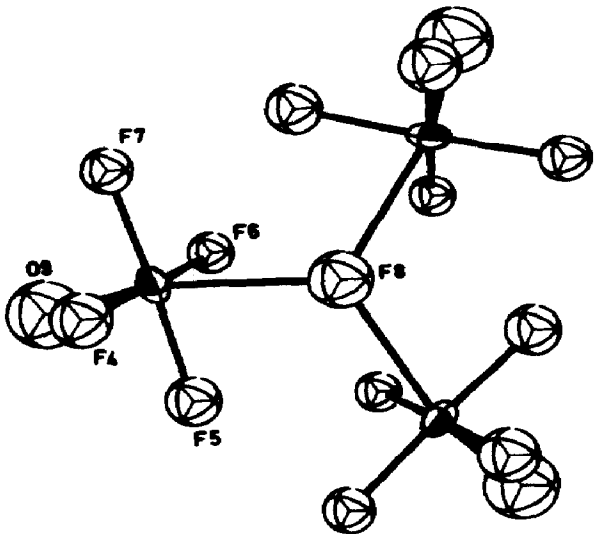


Figure 1. Structure of the $[(XeOF_4)_3F]^-$ anion with the atom numbering scheme viewed down the 3-fold axis: Xe-F distances 2.62Å and 1.92Å(average). (Reproduced by permission from Inorg. Chem., 24(1985)678).

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