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Chapter 8

NOBLE GASES

M.F.A.Dove

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.

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

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-Xe-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,

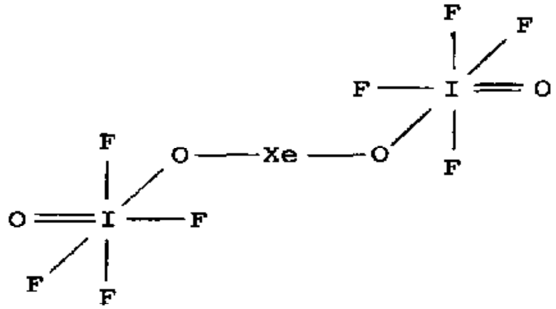
$$Me_nM \ + \ XeF_2 \rightarrow Me_nMF_2 \ + \ Xe \qquad \qquad ...(2)$$

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-$(TeF_5O)_4C_4F_6$ 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

$$\mathrm{Xe(OTeF_5)_2 + 2HOI(O)F_4 \rightarrow Xe(OI(O)F_4)_2 + 2HOTeF_5} \qquad ...(3)$$

$$\mathrm{Xe(OI(O)F_4)_2 \rightarrow \underbrace{IF_5 + IOF_3}_{\substack{\downarrow \\ \frac{1}{2}IF_5 + \frac{1}{2}IO_2F}} + Xe + 1.5O_2} \qquad ...(4)$$



(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

$$\mathrm{2CsF + 2XeF_4 \rightarrow Cs_2XeF_8 + XeF_2} \qquad ...(5)$$

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]

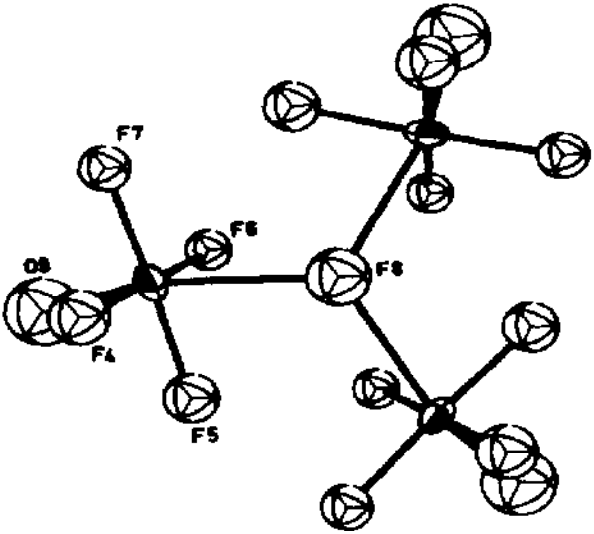


Figure 1. Structure of the $[(XeOF_4)_3F]^-$ anion with the atom numbering scheme viewed down the 3-fold axis: Xe-F distances 2.62Å and 1.92Å(average). (Reproduced by permission from Inorg. Chem., 24(1985)678).

REFERENCES

1 M.Guilhaus, A.G.Brenton, J.H.Beynon, M.Rabrenovic and P. von R.Schleyer, J. Chem. Soc., Chem. Commun., (1985)210.

2 L.Stein, J. Chem. Soc., Chem. Commun., (1985)1631.

3 J.H.Holloway, K.Lutar, A.Jesih and B.Zemva, J. Fluorine Chem., 29(1985)19,24.

4 Yu.M.Kiselev and V.B.Sokolov, Russ. J. Inorg. Chem., 29(1984)493.

5 Yu.M.Kiselev, S.A.Goryachenkov, L.I.Martynenko and V.I.Spitsyn, Dokl. Chem., (Engl. Transl.), 278(1984)291.

6 V.V.Nikulin, A.I.Popov, I.G.Zaitseva, M.V.Korobov, Yu.M.Kiselev and L.N.Sidorov, Russ. J. Inorg. Chem., 29(1984)21.

7 Yu.M.Kiselev, S.A.Goryachenkov and A.L.Il'inskii, Russ. J. Inorg. Chem., 30(1985)467.

8 Yu.M.Kiselev, S.A.Goryachenkov and L.I.Martynenko, Russ. J. Inorg. Chem., 29(1984)38.

9 S.A.Goryachenkov, N.E.Fadeeva, Yu.M.Kiselev, L.I.Martynenko and V.I.Spitsyn, Dokl. Chem., (Engl. Transl.), 278(1984)288.

10 D.F.Shellhamer, S.N.Graham, S.L.Carter, S.A.Shackelford and R.D.Chapman, J. Fluorine Chem., 29(1985)23.

11 A.M.Forster and A.J.Downs, Polyhedron, 4(1985)1625.

12 K.Alam and A.F.Janzen, J. Fluorine Chem., 27(1985)467.

13 C.J.Schack and K.O.Christe, J. Fluorine Chem., 27(1985)53.

14 T.R.G.Syvret and G.J.Schrobilgen, J. Fluorine Chem., 29(1985)31.

15 R.G.Syvret and G.J.Schrobilgen, J. Chem. Soc., Chem. Commun., (1985)1529.

16 Yu.M.Kiselev, S.A.Goryachenkov, L.I.Martynenko and V.I.Spitsyn, Dokl. Chem.,(Engl. Transl.), 278(1984)338.

17 J.H.Holloway, V.Kaucic, D.Martin-Rovet, D.R.Russell, G.J.Schrobilgen and H.Selig, Inorg. Chem., 24(1985)678.