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Chapter 8

NOBLE GASES

M.F.A.Dove

8.1 THE ELEMENTS.. 463
8.2 KRYPTON(II) AND XENON(II)........................ 463
8.3 XENON(IV).. 465
8.4 XENON(VI).. 465
REFERENCES.. 466

8.1 THE ELEMENTS

The structural properties of liquid and crystalline argon have been investigated using a molecular-mechanical model comprising 108 Lennard-Jones particles.[1] Calorimetric studies of liquid mixtures of xenon with HCl[2] and N_2O[3] have been carried out by Staveley et al: the enthalpy of mixing with liquid HCl could be satisfactorily reproduced using perturbation theory; on the other hand with liquid N_2O a positive azeotrope formation takes place. The dixenon cation, Xe_2^+, has been reported previously; Stern and Henderson[4] have shown that it is formed reversibly according to equation (1).

$$3Xe + XeF^+Sb_2F_{11}^- + 2SbF_5 \rightleftharpoons 2Xe_2^+Sb_2F_{11}^- \qquad ...(1)$$

The concentration of Xe_2^{2+} in this system was shown to be proportional to the $^3/_2$ power (approximately) of both the xenon pressure and of the $XeFSb_2F_{11}$ concentration, as well as the first power of the SbF_5 concentration. The authors infer that the Xe_2^+ cation is strongly bound in a complex with excess oxidant.

8.2 KRYPTON(II) AND XENON(II)

The 1:1 adduct between KrF_2 and BiF_5, which is as stable at room temperature as the SbF_5 analogue, has been investigated at low temperature by Raman spectroscopy. Three adducts of XeF_2 and BiF_5,

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2:1, 1:1 and 1:2, were also prepared and investigated similarly.[5] The results are of interest in connection with the relative amounts of covalent character in these compounds compared with the SbF_5 analogues : in all instances it was found that the BiF_5 compounds are more covalent.

The reaction of norbornene with XeF_2 in CH_2Cl_2 has been used as a mechanistic probe to elucidate the effect of catalyst and temperature (-61° to 25°C) on the liquid phase fluorination.[6] Up to seven products were obtained and the catalysts (HF, HF-py, BF_3, BF_3-Et_2O, and C_6F_5SH) had a marked effect on the reaction pathway : an analogous study of the fluorination of norbornadiene demonstrated that catalyst and temperature have less effect in this instance. Xenon(II) fluoride converts 1,3-diketones to mono- and di-fluoro products when the reaction is carried out in the presence of a mixture of the BF_3 complex of (cross-linked) polystyrene-4-vinylpyridine resin and of the uncomplexed resin.[7] The reaction of enol acetates with XeF_2 in the presence of anhydrous HF gave α-fluoroketones. One of the three possible L-3,4-dihydroxyfluorophenylalanines was found after workup following fluorination of L-3-methoxy-4-hydroxyphenylalanine by XeF_2 in CH_2Cl_2 :[8] the 6-fluoro compound was isolated in 25% yield.

High rates of surface etching of Ge and Si single crystals by gaseous XeF_2 have been reported by Baklanov et al.[9] The rate of attack does not depend upon either the crystallographic orientation of the crystal surface (over the temperature range 5°-90°C) or the vapour pressure (5×10^{-2} - 1.4 torr) of XeF_2 used.

Holloway and Schrobilgen[10] have presented ^{19}F and ^{129}Xe n.m.r. evidence for the structures of the adducts formed between XeF_2 and $nMOF_4$, M=Mo or W, n=1, 2, 3 and 4. Interestingly some of these adducts contain XeF...M bridges which are non-labile on the n.m.r. time scale at low temperatures in BrF_5 or SO_2ClF solutions : these complexes undergo solvolysis in HSO_3F at -80°C, according to equations (2) and (3), on the basis of n.m.r. studies. A group of

$$FXeFMOF_4 + HSO_3F \longrightarrow F\text{-}Xe\text{-}OS(O)(F)O\text{-}MF_4O + HF \qquad ...(2)$$

$$FXeOS(O)(F)OMF_4O \rightleftharpoons FXeOSO_2F + MOF_4 \qquad ...(3)$$

adducts $XeF_2.mWOF_4$, m=2 or 3, were found to be partially iomerised in SO_2ClF, e.g. to the O-bridged compound (<u>1</u>).

$$FXe{-}O{-}WF_4{-}F{-}W(O)F_3{-}F{-}WF_4O$$

(1)

Jacob has shown that $(F_3Si)_2O$ is slowly oxidised by KrF_2 and XeF_2; reaction (4) is complete in 8h or less at 25°C (Ng=Kr or Xe).

$$NgF_2 + (SiF_3)_2O \longrightarrow Ng + \tfrac{1}{2}O_2 + 2SiF_4 \qquad ...(4)$$

8.3 XENON(IV)

Adducts with 1 or $2BiF_5$ and XeF_4 have been prepared and their low-temperature Raman spectra discussed by Gillespie at al.[5] Xenon(IV) fluoride reacts slowly with $(SiF_3)_2O$, equation (5).[11]

$$XeF_4 + 2(SiF_3)_2O \xrightarrow[25^{\circ}C]{ca.1d} Xe + O_2 + 4SiF_4 \qquad ...(5)$$

8.4 XENON(VI)

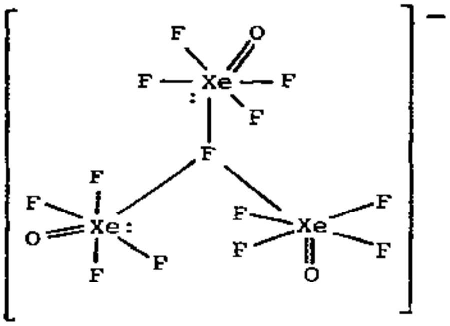
The hexafluoride can be converted conveniently to $XeOF_4$ in the gas-phase reaction (6).[11] This reaction is more controllable

$$XeF_6 + (SiF_3)_2O \longrightarrow XeOF_4 + 2SiF_4 \qquad ...(6)$$

than other sources of oxygen, such as H_2O or SiO_2/HF. The reaction with excess $(SiF_3)_2O$ requires several days and leads to total reduction of $XeOF_4$ to Xe and oxygen.[11]

Two new oxofluoroanions of xenon(VI) have been synthesised and characterised by Schrobilgen et al.[12] in the course of a study of the reactions between CsF and excess liquid $XeOF_4$. The product of the room temperature reaction loses $XeOF_4$ at 0°C to yield $CsF.3XeOF_4$. The 1:1 adduct could be prepared from this by the loss of $2XeOF_4$ at room temperature. The Raman spectra of $XeOF_5^-$ ion is consistent with C_s symmetry around Xe so that the lone pair is presumably stereochemically active. The structure proposed for the anion in the 1:3 adduct, (2), has three equivalent $XeOF_4$ units bonded to the fluoride ion.

The first example of the fluorination of 1,3-diketones to the 2-fluoroproduct has been described by Yemul and Kagan.[13] They used the graphite-XeF_6 intercalation compound, $C_{19}XeF_6$, as the fluorinating agent : typically the reaction takes place at room temperature for 24h under which conditions monoketones do not react.



(2)

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