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Chapter 8

NOBLE GASES

M.F.A.Dove

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, 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>).

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

(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]

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

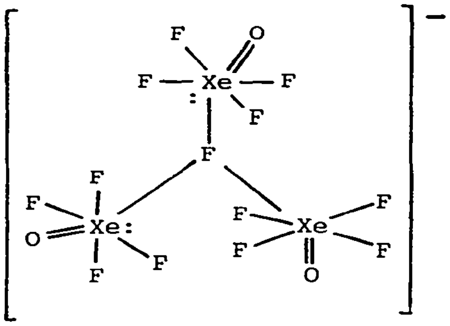
8.4 XENON(VI)

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

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

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)

REFERENCES

1 A.E.Galashev and V.P.Skripov, J. Struct. Chem., 21(1980)158.
2 L.Q.Lobo, L.A.K.Staveley, P.Clancy and K.E.Gubbins, J. Chem. Soc. Faraday Trans. I, 76(1980)174.
3 J.R.S.Machado, K.E.Gubbins, L.Q.Lobo and L.A.K.Staveley, J. Chem. Soc. Faraday Trans. I, 76(1980)2496.
4 L.Stein and W.H.Henders on, J. Am. Chem. Soc., 102(1980)2856.
5 R.J.Gillespie, D.Martin and G.J.Schrobilgen, J. Chem. Soc. Dalton Trans., (1980)1898.
6 A.Gregorčič and M.Zupan, Bull. Chem. Soc. Jpn., 53(1980)1085.
7 B.Zaja and M.Zupan, J. Chem. Soc. Chem. Commun., (1980)759.
8 G.Firnau, R.Chirakal, S.Sood and S.Garnett, Can. J. Chem., 58(1980)1449.
9 M.R.Baklanov, S.M.Repinskii and A.V.Rzhanov, Doklady Chem., 253(1980)375.
10 J.H.Holloway and G.J.Schrobilgen, Inorg. Chem., 19(1980)2632.
11 E.Jacob, Z. Naturforsch., 35b(1980)1088.
12 G.J.Schrobilgen, D.Martin-Rovet, P.Charpin and M.Lance, J. Chem. Soc. Chem. Commun., (1980)894.
13 S.S.Yemul, H.B.Kagan and R.Setton, Tetrahedron Lett., 21(1980)277.