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Chapter 8

NOBLE GASES

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8.1 XENON(O)

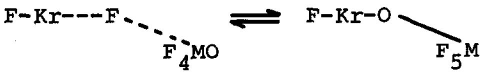
The sensitivity of the nuclear magnetic shielding of the ^{129}Xe nucleus to its physical environment makes it possible to distinguish between atoms in small and large clathrate deuteriohydrate cages.[1] The occupancy ratio of the two cages is more in favour of the larger one than is predicted by existing models of guest-host interactions in such hydrates.

8.2 KRYPTON(II) AND XENON(II)

Solutions of KrF_2 and $MoOF_4$ in SO_2ClF are stable only below 0°C and Holloway and Schrobilgen[2] have successfully characterised $KrF_2.nMoOF_4$ F-bridged adducts (n = 1,2 or 3) in these solutions by ^{19}F n.m.r. studies at -121°C. These adducts are significantly more stable in solution than the WOF_4 analogues which decompose even at -100°C according to equation (1) : the μ-fluorine bridged

$$KrF_2 + WOF_4 \longrightarrow Kr + \tfrac{1}{2}O_2 + WF_6 \qquad ...(1)$$

complex $KrF_2.WOF_4$ was characterised by ^{19}F n.m.r. spectroscopy, however there was no evidence for 1:2 or higher complexes. The general instability of the W complexes and especially of the 1:2 and higher complexes was rationalised in terms of equilibrium (2),



$$F{-}Kr{-}{-}{-}F\cdots F_4MO \rightleftharpoons F{-}Kr{-}O{-}F_5M \qquad ...(2)$$

which has a well established analogue in xenon(II) chemistry. Thus the authors concluded that Kr-O bonded systems are unlikely. Indeed, all attempts by Jacob et al.[3] to generate $Kr(OTeF_5)_2$ from $B(OTeF_5)_3$ or $HOTeF_5$ and KrF_2 have failed : however the formation of BF_3 and $F_5TeOOTeF_5$ from $B(OTeF_5)_3$ even at -196°C can be interpreted as evidence for the intermediacy of a $Kr-O-TeF_5$ derivative. The Raman spectra of the solid adducts with $MoOF_4$ and WOF_4 were recorded at -108°C (XeF_2 adducts) and -196°C (KrF_2 adducts) respectively and assignments were presented.[2]

A polymeric xenon compound, which is probably oxygen-bonded, has been reported:[4] it was prepared by reaction (3) carried out

$$XeF_2 + cis\text{-}(HO)_2TeF_4 \longrightarrow \frac{1}{n}(\text{-}Xe\text{-}OTeF_4O\text{-})_n + 2HF \qquad ...(3)$$

in $C_4F_9SO_2F$ at 20°C. The new xenon(II) compound $Xe(N(SO_2F)_2)_2$ has been obtained as one of the products of reaction of XeF_2 with $HN(SO_2F)_2$ at low temperatures.[5] The ratio of the new compound to $FXeN(SO_2F)_2$ in the mixture was controlled by the reaction ratio. Thus a 1:2 molar ratio of reagents yielded 20% of the bis compound based on XeF_2. The thermal decomposition of the bis compound even at 0° in $CFCl_3$ gives rise to the free radical $N(SO_2F)_2$ (q.v.). The action of XeF_2 on other nitrogen compounds was also investigated; HNF_2 gave N_2F_4 + HF + Xe, perfluorosuccinimide underwent extensive degradation whereas $(CF_3)_2NH$ and $(CF_3)_2C{=}NH$ were inert.

The previously reported $XeOTeF_5^+$ cation has been more fully characterised by Raman spectroscopy of its AsF_6^- and $Sb_2F_{11}^-$ salts and by multinuclear (^{19}F, ^{125}Te and ^{129}Xe) n.m.r. spectroscopy.[6] Reaction of the AsF_6^- salt with BrF_5 has been shown to yield the novel cations $FXeFXeOTeF_5^+$ and $XeF_2.BrOF_2^+$ via the series of reactions (4)-(6). In addition evidence was also

$$2XeOTeF_5^+AsF_6^- + BrF_5 \xrightarrow{-48^\circ C} TeF_6 + XeF_2XeOTeF_5^+AsF_6^- + BrOF_2^+AsF_6^- \qquad ...(4)$$

$$XeF_2XeOTeF_5^+AsF_6^- + BrF_5 \xrightarrow{-48^\circ C} TeF_6 + Xe_2F_3^+AsF_6^- + BrOF_3 \qquad ...(5)$$

$$Xe_2F_3{}^+AsF_6{}^- + BrOF_3 + BrOF_2{}^+AsF_6{}^- \xrightarrow{RT} 2[XeF_2.BrOF_2{}^+AsF_6{}^-] \quad ...(6)$$

provided for the formation of the $XeOSO_2F^+$ cation in reaction (7).

$$XeOTeF_5{}^+ + HOSO_2F \rightleftharpoons HOTeF_5 + XeOSO_2F^+ \quad ...(7)$$

The synthesis of ^{18}F-labelled XeF_2 has been investigated by Schrobilgen et al:[7] neutron irradiated $^6Li_2CO_3$ was converted to essentially anhydrous HF and exchange between this and XeF_2 was allowed to take place. The authors forsee that $[^{18}F]XeF_2$ will become a highly useful intermediate for the preparation of a variety of medically important ^{18}F-labelled compounds.

Xenon difluoride adds efficiently at room temperature to hexafluoroisopropylideneimidosulphenyl isocyanate, $(CF_3)_2C=N-S-N=C=O$, in a 1,3 manner to form $(CF_3)_2CFN=SF(NCO)$ and in a 1,5 manner to form $(CF_3)_2CFN=S=N-COF$;[8] in the presence of BF_3 the principal unfragmented product is the S(VI) compound $(CF_3)_2CFN=SF_2=NCOF$. The XeF_2-fluorination of 2-bromo-4,5-dimethyphenol has been investigated:[9] the yield of monofluorinated products was higher in the presence of BF_3-etherate than with HF or CF_3CO_2H.

The reactions of excess XeF_2 with some ammonium hexafluorometallates, $(NH_4)_2MF_6$ (M = Ti, Zr or Hf) and $(NH_4)_3M'F_6$ (M' = V, Cr, Mn or Fe) and with NH_4MnF_3 have been described by Slivnik et al.[10] Reactions (8)-(10) are representative of some of the processes which occurred. Xenon(II) fluoride doped polyacetylene film shows an enhanced electrical conductivity ($70\Omega^{-1}cm^{-1}$);[11] this decreases to less than $10^{-4}\Omega^{-1}cm^{-1}$ when the volatiles are removed at which stage the composition corresponds to $[CH_{0.90}(XeF_2)_{0.045}F_{0.36}]_x$.

$$(NH_4)_2TiF_6 \xrightarrow{180^oC} XeF_2.TiF_4 \quad ...(8)$$

$$(NH_4)_3VF_6 \xrightarrow{70^oC} (NH_4)_3VF_8 \quad ...(9)$$

$$NH_4MnF_3 \xrightarrow{60^oC} NH_4MnF_4 \quad ...(10)$$

8.3 XENON(IV) AND XENON(VI)

Details of the synthesis and handling problems of $Xe(OTeF_5)_4$, $Xe(OTeF_5)_6$ and $XeO(OTeF_5)_4$ have appeared.[3] From X-ray powder diffraction studies it has been inferred that $Xe(OTeF_5)_6$ is monomeric since it is isostructural and nearly isodimensional with $Te(OTeF_5)_6$. Evidence for the existence of even less stable $XeF_n(OTeF_5)_{6-n}$ was also presented. However a mixture of $XeOF_4$ and $XeO(OTeF_5)_4$ were shown to undergo ligand exchange readily to form a stable mixture of all possible intermediates including both possible isomers of $XeOF_2(OTeF_5)_2$.

The controlled reaction between NH_4MnF_3 and XeF_6, initially at 0°C and then at 60°C, to complete the processes, has yielded a solid product containing NH_4^+, Xe and Mn(IV).[12] Neither N_2 nor nitrogen fluorides were detectable during the reaction. On the basis of chemical analysis, magnetic susceptibility measurements and vibrational spectroscopy the solid reaction product was formulated as $NH_4^+XeF_5^+MnF_6^{2-}$. Two new compounds have been synthesised from the XeF_6-VF_5 system:[13] these, the 1:1 and 1:2 compounds, are in addition to the already known 2:1 compound. From their Raman spectra it was concluded that ionic character decreases with increasing VF_5 content; thus the 2:1 compound (m.p. 97°C) is formulated as $Xe_2F_{11}^+VF_6^-$.

Polyacetylene film inflames on contact with liquid $XeOF_4$:[11] exposure to the vapour, 1.5 Torr, causes the electrical conductivity to rise significantly (to $50\Omega^{-1}cm^{-1}$ for the composition $[CH(XeOF_4)_{0.025}]_x$).

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