Coordination Chemistry Reviews, 49 (1983) 471–475
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

Chapter 8

NOBLE GASES

M.F.A.Dove

8.1 XENON(O)

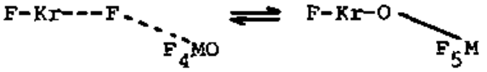
The sensitivity of the nuclear magnetic shielding of the ^{129}Xe nucleus to its physical environment makes it possible to distinguish between atoms in small and large clathrate deuteriohydrate cages.[1] The occupancy ratio of the two cages is more in favour of the larger one than is predicted by existing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

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

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),



$$F\text{-}Kr\text{---}F\cdots MOF_4 \rightleftharpoons F\text{-}Kr\text{-}O\text{-}MF_5 \qquad \text{...(2)}$$

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

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

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

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

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

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

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

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

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

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

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 $[CH_{0.90}(XeF_2)_{0.045}F_{0.36}]_x$.

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 $0^{o}C$ and then at $60^{o}C$, 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. $97^{o}C$) 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 $[CH(XeOF_4)_{0.025}]_x$).

REFERENCES

1 J.A.Ripmeester and D.W.Davidson, J. Mol. Struct., 75(1981)67.

2 J.H.Holloway and G.J.Schrobilgen, Inorg. Chem., 20(1981)3363.

3 E.Jacob, D.Lentz, K.Seppelt and A.Simon, Z. Anorg. Allg. Chem., 472(1981)7.

4 B.Pötter, D.Lentz, H.Pritzkow and K.Seppelt, Angew. Chem. Int. Ed. Engl., 20(1981)1036.

5 D.D.DesMarteau, R.D.LeBlond, S.F.Hossain and D.Nothe, J. Am. Chem. Soc., 103(1981)7734.

6 N.Keller and G.J.Schrobilgen, Inorg. Chem., 20(1981)2118.

7 G.J.Schrobilgen, G.Firnau, R.Chirakal and E.S.Garnett, J. Chem. Soc. Chem. Commun., (1981)198.

8 H.Steinbeisser and R.Mews, J. Fluorine Chem., 17(1981)505.

9 H.Kondstaal and C.Olieman, Rec., 100(1981)246.

10 J.Slivnik, B.Družina and B.Žemva, Z. Naturforsch., 36b(1981) 1457.

11 H.Selig, A.Pron, M.A.Druy, A.G.McDiarmid and A.J.Heeger, J. Chem. Soc. Chem. Commun., (1981)1288.

12 B.Žemva and J.Slivnik, J. Fluorine Chem., 17(1981)375.

13 A.Jesih, B.Žemva and J.Slivnik, J. Fluorine Chem., 19(1982)221.