Coordination Chemistry Reviews, 103 (1990) 266–270
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 8

THE NOBLE GASES

I.G.Southerington

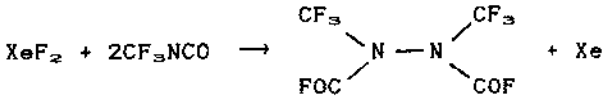
0010-8545/90/$03.50

8.1 XENON(II) AND KRYPTON(II)

The chemistry of xenon(II) forms the bulk of a review by Holloway[1] celebrating the first 25 years of noble gas chemistry. Smaller sections are also dedicated to the chemistry of krypton and radon.

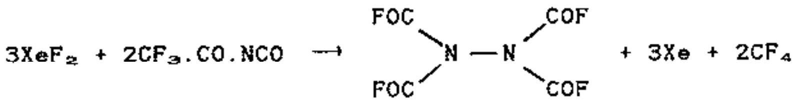
Brassington and Edwards[2] have recorded the Raman spectrum of XeF_2 in both the solid and gaseous phases, along with a determination of the Xe-F force constants using the SV.FF approximation.

The reactive versatility of XeF_2 has again been demonstrated. An excess of XeF_2 with SnF_2 at 140°C leads to formation of two new fluorostannates, i.e. $3XeF_2.4SnF_4$ and $XeF_2.2SnF_4$.[3] On the basis of infrared spectroscopy, the latter is formulated as an XeF^+ salt of a polymeric anion, while the former is considered to be a molecular adduct of XeF_2 and the 1:2 compound. The reaction of XeF_2 with isocyanates and related compounds has been shown to give the corresponding fluorocarbonyl hydrazides.[4] Examples are shown in equations (1), (2) and (3). The



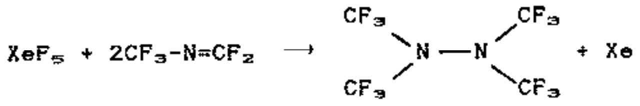
$$XeF_2 + 2CF_3NCO \longrightarrow (CF_3)(FOC)N{-}N(CF_3)(COF) + Xe$$

...(1)



$$3XeF_2 + 2CF_3.CO.NCO \longrightarrow (FOC)_2N{-}N(COF)_2 + 3Xe + 2CF_4$$

...(2)



$$XeF_5 + 2CF_3\text{-}N{=}CF_2 \longrightarrow (CF_3)_2N{-}N(CF_3)_2 + Xe$$

...(3)

fluorinating ability of XeF_2 has been demonstrated in the reaction with CrO_2F_2 (equation 4), which proceeds in high yield at temperatures up to 278°C producing the first crystalline sample of $CrOF_3$.[5] Fluorination also occurs when XeF_2 and

$$XeF_2 + 2CrO_2F_2 \longrightarrow 2CrOF_3 + Xe + O_2 \qquad ...(4)$$

$$3XeF_2 + 2SeOF_2 \longrightarrow Xe(OSeF_5)_2 + 2Xe \qquad ...(5)$$

$SeOF_2$ react at -78°C in a 3:2 molar ratio (equation 5): the pale yellow crystalline product, $Xe(OSeF_5)_2$, has been studied by both ^{19}F and ^{129}Xe n.m.r. spectroscopy.[6] The former shows a pattern typical of AB_4 type species, while the ^{129}Xe spectrum shows the expected nine lines due to coupling with eight equivalent equatorial fluorine atoms.

Oxidative addition of F_5TeO radicals created thermally or photolytically from $Xe(OTeF_5)_2$ to metal halides yields new pentafluorooxotellurate(VI) complexes (equation 6).[7]

$$E\text{-}X + Xe(OTeF_5)_2 \longrightarrow Xe + EX(OTeF_5)_2 \qquad ...(6)$$

The Xe-N bonded complex, $FXeN(SO_2F)_2$, exhibits fluorine ion donor properties leading to three new adducts, namely $FXeN(SO_2F)_2.AsF_5$, $FXeN(SO_2F)_2.3SbF_5$ and $2FXeN(SO_2F)_2.AsF_5$.[8] All compounds were enriched with 30% ^{15}N and studied by ^{15}N, ^{19}F and ^{129}Xe n.m.r. and Raman spectroscopy. The results point to ionic formulations for all three species, i.e. $XeN(SO_2F)_2{}^+AsF_6{}^-$, $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$ and $\{F[XeN(SO_2F)_2]_2\}^+AsF_6{}^-$. An X-ray structure determination for $[XeN(SO_2F)_2]^+Sb_3F_{16}{}^-$ at -64°C showed the presence of discrete molecules with an Xe-N distance of

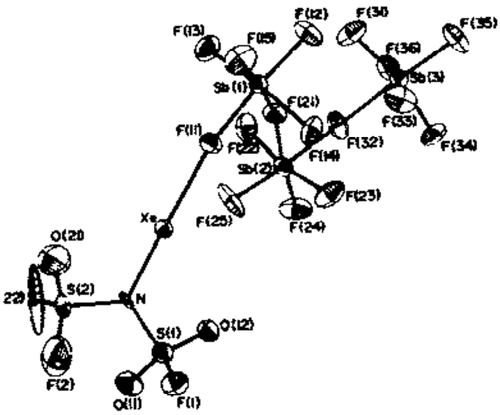


Figure 1. Structure of $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$ (reproduced by permission from Inorg. Chem., 25(1986)563).

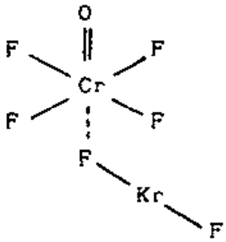
202.1pm in the $[XeN(SO_2F)_2]^+$ cation (see Figure 1). This distance is much shorter than the Xe-N separation in $FXeN(SO_2F)_2$ (220pm). The $Sb_3F_{16}^-$ anion is cis-fluorine bridged and weakly bonded to the cation with an Xe...F distance of 245.8pm.

KrF_2 is also a useful fluorinating agent, producing volatile PuF_6 from PuF_4 at low temperatures.[9] The same paper also describes the use of gaseous KrF_2 to bring about the volatization of uranium and neptunium from solid substrates (equation 7).

$$KrF_{2(g)} + MF_{4(s)} \xrightarrow{\text{anhyd. HF}} MF_{6(g)} + Kr \qquad \ldots(7)$$

(M = Np,U)

KrF_2 has also been employed as a fluorinating agent in preparing $CrOF_4$ from CrO_2F_2.[10] The reaction product is a relatively strong Lewis acid forming an unstable 1:1 covalent adduct with KrF_2 (1), which completely dissociates in SO_2ClF solution.



(1)

8.2 XENON(IV) AND XENON(VI)

When XeF_2 and cesium fluoride separated by a layer of manganese(II) fluoride, are heated in a reactor to 300-350°C, the product is cesium octafluoroxenate(IV) formulated as Cs_4XeF_8.[11]

The reactivity of various hydrazinium fluorouranates(IV) towards XeF_2 and XeF_6 has been described by Druzina and Zemva.[12] With XeF_2, the major products are $(NH_4)_2XeF_6$, nitrogen, xenon, HF and UF_6. Similar products are given for reactions with XeF_6, along with the adduct $XeF_6.UF_5$.

REFERENCES

1 J.H.Holloway, Chem. Br., 23(1987)658.

2 N.J.Brassington and M.G.M.Edwards, J. Mol. Struct., 162(1987)69.

3 B.Druzina and B.Zemva, J. Fluorine Chem., 34(1986)233.

4 W.Sundermeyer and M.Witz, J. Fluorine Chem., 34(1986)251.

5 M.McHughes, R.D.Willett, H.B.Davis and G.L.Gard, Inorg. Chem., 25(1986)426.

6 K.Seppelt, D.Lentz and G.Kloeter, Inorg. Synth., 24(1986)27.

7 F.Sladky, Inorg. Synth., 24(1986)33.

8 R.Faggiani, D.K.Kennepohl, C.J.L.Lock and G.J.Schrobilgen, Inorg. Chem., 25(1986)563.

9 L.B.Asprey, P.G.Eller and S.A.Kinkead, Inorg. Chem., 25(1986)670.

10 K.O.Christe, W.W.Wilson and R.A.Bougon, Inorg. Chem., 25(1986)2163.

11 M.Y.Kiselev, S.A.Goryachenkov and L.I.Martynenko, Otkrytiya, Izobert. 1986, (1), III; C.A., 104(1986) P151823n.

12 B.Druzina and B.Zemva, Vestn. Slov. Kem. Drus., 1986, 33(1)1; C.A: 105(1987) 107344d.