

Chapter 8

NOBLE GASES

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8.1 THE ELEMENTS

The behaviour of supercritical xenon as a solvent has been investigated at pressures up to 225atm. with naphthalene as the solute :¹ this study is claimed to be the first to demonstrate that xenon exhibits enhanced solvent properties comparable to those of methane, ethene and carbon dioxide. The n.m.r. relaxation times of ^{131}Xe ($I = 3/2$) in a variety of solvents at room temperature have been measured by Stengle et al.² Relaxation in polar solvents is relatively rapid and the electrostatic model of Hertz provides a good semiquantitative picture of the interactions in such media.

Stein³ has attempted to repeat the experiments published by Avrorin et al in 1981 in which higher fluorides of radon as well as a water-soluble oxide, RnO_3 , were reported. He concludes that their interpretation did not take account of the tendency of trace amounts of ^{222}Rn to be trapped in suspended solids. Thus he reports that not more than 0.2% Rn remained in solution after hydrolysis of $(\text{RnF})_2\text{NiF}_6$.

8.2 KRYPTON(II) AND XENON(II)

An improved synthesis of $\text{KrF}^+\text{MF}_6^-$, $M = \text{As}$ or Sb , and the existence of a $\text{Kr}_2\text{F}_3^+ \cdot \text{BF}_4^- \cdot n(\text{KrF}_2)$ adduct have been reported:⁴ the reactivity of KrF^+ towards NF_3 , ClF_5 and BrF_5 were also examined

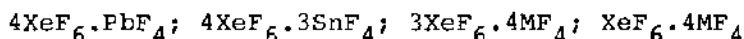
and compared with the reactivity of PtF_6 . Addition reactions of $\text{Xe}(\text{OTeF}_5)_2$ with a number of mono-fluoro-olefins produce fluorocarbons with two OTeF_5 substituents.⁵ The reaction of HCN with $\text{Xe}(\text{OMF}_5)_2$, $\text{M} = \text{Se or Te}$, yields $\text{F}_5\text{M-N=C=O}$, reaction (1), presumably via F_5MOXeCN and F_5MOCN .⁶ This route provides the



first synthesis of the selenium(VI) isocyanate. Fluorination of the $-\text{PF}_2$ ligand in $\text{Ir}(\text{CO})\text{Cl}_2(\text{PEt}_3)_2\text{PF}_2$ by XeF_2 in CH_2Cl_2 at 280K converts the complex to one containing the $-\text{PF}_4$ ligand.⁷ Dimethyl sulphide is fluorinated by XeF_2 in non-acidic media under carefully controlled conditions to give a product best formulated as $\text{Me}_2\text{SCH}_2\text{SMe}^+\text{H}_n\text{F}_{n+1}^-$.⁸ In the presence of an HF-sink, e.g. CsF , the sulphur containing product was $(\text{CH}_2\text{F})\text{SMe}$. However in liquid HF the cation Me_2SF^+ was formed at -23°C .

8.3 XENON(IV) AND (VI)

A series of mixed fluoro(pentafluoroorthotellurato) derivatives of the xenon compounds, XeF_4 , XeOF_4 and XeO_2F_2 , have been produced for the first time by Schumacher and Schrobilgen.⁹ They characterised the products by low temperature Raman and by n.m.r. spectroscopy. The new xenon(VI) fluorometallates ($\text{M} = \text{Sn or Pb}$)



have been isolated and characterised for the first time.¹⁰ From the vibrational spectra the 4:1 compounds are formulated as $(\text{Xe}_2\text{F}_{11})^+{}_2\text{MF}_6^{2-}$ and the 1:4 compounds as $\text{XeF}_5^+(\text{M}_4\text{F}_{17})^-$.

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