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Chapter 8

NOBLE GASES

M.F.A. Dove

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.

Stein[3] 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 $(RnF)_2NiF_6$.

8.2 KRYPTON(II) AND XENON(II)

An improved synthesis of $KrF^+MF_6^-$, M = As or Sb, and the existence of a $Kr_2F_3^+.BF_4^-.n(KrF_2)$ adduct have been reported:[4] the reactivity of KrF^+ towards NF_3, ClF_5 and BrF_5 were also examined

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and compared with the reactivity of PtF_6. Addition reactions of $Xe(OTeF_5)_2$ with a number of mono-fluoro-olefins produce fluorocarbons with two $OTeF_5$ substituents.[5] The reaction of HCN with $Xe(OMF_5)_2$, M = Se or Te, yields $F_5M\text{-}N{=}C{=}O$, reaction (1), presumably via $F_5MOXeCN$ and F_5MOCN.[6] This route provides the

$$Xe(OMF_5)_2 + HCN \rightarrow HOMF_5 + F_5MNCO \qquad \ldots(1)$$

first synthesis of the selenium(VI) isocyanate. Fluorination of the $-PF_2$ ligand in $Ir(CO)Cl_2(PEt_3)_2PF_2$ by XeF_2 in CH_2Cl_2 at 280K converts the complex to one containing the $-PF_4$ ligand.[7] Dimethyl sulphide is fluorinated by XeF_2 in non-acidic media under carefully controlled conditions to give a product best formulated as $Me_2SCH_2SMe^+H_nF_{n+1}^-$.[8] In the presence of an HF-sink, e.g. CsF, the sulphur containing product was $(CH_2F)SMe$. 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 (M = Sn or Pb)

$$4XeF_6.PbF_4;\ 4XeF_6.3SnF_4;\ 3XeF_6.4MF_4;\ XeF_6.4MF_4$$

have been isolated and characterised for the first time.[10] From the vibrational spectra the 4:1 compounds are formulated as $(Xe_2F_{11}^+)_2MF_6^{2-}$ and the 1:4 compounds as $XeF_5^+(M_4F_{17}^-)$.

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