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Chapter 8

NOBLE GASES

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8.1 THE ELEMENTS

The adsorption of Xe on Pt supported on NaY-zeolite at 25°C has been investigated by ^{129}Xe n.m.r. spectroscopy.[1] The solubility of the noble gases in 1,4-dioxan at 101kPa over the temperature range 285-303K has been reported.[2] Liquid Xe is a useful solvent for e.s.r. studies of reactive free radicals, e.g. reactions (1) and (2): the g-factors of many types of radical are not the same in Xe as in normal solvents.[3] Cook and Roberts did not detect any Xe-based radicals.

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \qquad ...(1)$$

$$Bu^tO\cdot + CH_2{=}CH{-}CH_3 \rightarrow Bu^tOH + CH_2{=}CH{-}CH_2^{\cdot} \qquad ...(2)$$

The UV photolysis of $Cr(CO)_6$ in liquid Xe/N_2 mixtures at 183K has been shown by i.r. spectroscopy to generate the mixed carbonyl dinitrogen species, $Cr(CO)_{6-x}(N_2)_x$, x = 1 to 5.[4] The compound with x = 1 was found to be unstable thermally in liquid Xe at -35°C, whereas the x = 5 compound is unstable even at -90°C. The presence of xenon in the first coordination sphere of $Cr(CO)_5$ has been reported for the first time by Turner and coworkers.[5] It was produced by the photolysis of $Cr(CO)_6$ in liquified Xe or Kr doped with Xe and detected by i.r. spectroscopy. The half-life of $[Cr(CO)_5Xe]$ in such solutions is ca. 2s at -98°C.

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8.2 KRYPTON(II) AND XENON(II)

Fluorination of methionine or methionylglycine derivatives with XeF_2 in MeCN occurs exclusively at the methylthio position, in 70-90% yield under carefully controlled conditions.[6] The synthesis of ^{15}N-enriched $Xe[N(SO_2F)_2]_2$ has enabled Schumacher and Schrobilgen[7] to characterise this compound by both ^{15}N and ^{129}Xe n.m.r. spectroscopy. Three possible isotopic isomers were identified and the presence of two equivalent Xe-N bonds inferred. The dissociation of $F[XeN(SO_2F)_2]_2{}^+AsF_6{}^-$ in solution was also investigated and the formation of $Xe[N(SO_2F)_2]_2$ in SO_2ClF established. Thermal analysis studies of XeF_2 have shown that above 350°C disproportionation occurs to Xe and XeF_4.[8] The reaction of XeF_2 with $Cs_3M^{III}F_6$, M = Ce, Pr. Tb, Nd, Dy or Er, has been studied thermogravimetrically.[9] The formation of $Cs_3M^{IV}F_7$ occurred in the temperature range 115°C (for Ce) to 382°C (for Nd).

The X-ray photoelectron spectra of core levels of KrF_2, XeF_4 and XeF_6 have been obtained. Satellites on the low kinetic energy side of the core levels have been assigned to monopole-allowed shake-up transitions by using Xα-SW hole state and atomic model calculations.[10] An Xα-SW calculation on the KrF_2 ground state gives good agreement with the experimental valence-bond energies.

8.3 XENON(IV) AND (VI)

Photolysis of XeF_6 is said to cause complete dissociation to XeF_4 and F_2.[11]

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