

Chapter 8

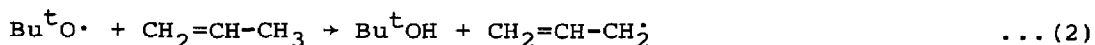
NOBLE GASES

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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. The UV photolysis of $\text{Cr}(\text{CO})_6$ in liquid Xe/ N_2 mixtures at 183K has been shown by i.r. spectroscopy to generate the mixed carbonyl dinitrogen species, $\text{Cr}(\text{CO})_{6-x}(\text{N}_2)_x$, $x = 1$ 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 $\text{Cr}(\text{CO})_5$ has been reported for the first time by Turner and coworkers.⁵ It was produced by the photolysis of $\text{Cr}(\text{CO})_6$ in liquified Xe or Kr doped with Xe and detected by i.r. spectroscopy. The half-life of $[\text{Cr}(\text{CO})_5\text{Xe}]$ in such solutions is ca. 2s at -98°C.

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 $\text{Xe}[\text{N}(\text{SO}_2\text{F})_2]_2$ has enabled Schumacher and Schrobilgen⁷ 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 $\text{F}[\text{XeN}(\text{SO}_2\text{F})_2]_2^+\text{AsF}_6^-$ in solution was also investigated and the formation of $\text{Xe}[\text{N}(\text{SO}_2\text{F})_2]_2$ 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 $\text{Cs}_3\text{M}^{\text{III}}\text{F}_6$, M = Ce, Pr, Tb, Nd, Dy or Er, has been studied thermogravimetrically.⁹ The formation of $\text{Cs}_3\text{M}^{\text{IV}}\text{F}_7$ 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 $\text{X}\alpha$ -SW hole state and atomic model calculations.¹⁰ An $\text{X}\alpha$ -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

REFERENCES

- 1 T.Ito, L.-C. de Menorval, J. Chem. Phys., 30(1983)573.
- 2 M.A.Gallardo, J.S.Urieta and C.G.Losa, J. Chim. Phys., 30(1983)621.
- 3 M.D.Cook and B.P.Roberts, J. Chem. Soc., Chem. Commun., (1983)264.
- 4 J.J.Turner, M.B.Simpson, M.Poliakoff, W.B.Maier and M.A. Graham, Inorg. Chem., 22(1983)911.
- 5 M.B.Simpson, M.Poliakoff, J.J.Turner, W.B.Maier and J.G.McLaughlin, J. Chem. Soc., Chem. Commun., (1983)1355.
- 6 A.F.Janzen, P.M.C.Wang and A.E.Lemire, J. Fluorine Chem., 22(1983)557.
- 7 G.A.Schumacher and G.J.Schrobilgen, Inorg. Chem., 22(1983)2178.
- 8 Yu.M.Kiselev and S.A.Goryachenko, Russ. J. Inorg. Chem., 28(1983)9.
- 9 M.Kiselev, S.A.Goryachenkov and L.I.Martynenko, Russ. J. Inorg. Chem., 28(1983)651.
- 10 G.M.Bancroft, D.J.Bristow, J.S.Tse, and G.J.Schrobilgen, Inorg. Chem., 22(1983)2673.
- 11 K.Lutar and J.Slivnik, J. Fluorine Chem., 23(1983)430.