

Chapter 8

THE NOBLE GASES

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8.1 THE ELEMENTS

The He-benzene and He₂-benzene van der Waals complexes have been investigated spectroscopically under conditions (rotational cooling achieved by supersonic expansion) in which over 95% of the molecules are in the lowest rovibronic level.¹ In both complexes the helium atoms are found to lie in the C₆ symmetry axis away from the plane of the benzene ring. Weiss et al.² have shown that the novel inclusion compounds CdPt(CN)₆.1.046Kr and CdPt(CN)₆.1.128Xe are formed when crystals of the host compound were grown in the presence of the noble gas at 64 bar pressure : only half of the 4.7Å diameter cavities are occupied by guest atoms. The concentration of radon in a variety of geothermal sources can be related to reservoir characteristics and operating conditions.³

Hawkins, Falconer and Bartlett⁴ have compiled a bibliography of the noble gases and their compounds covering all the papers published in years 1962-1976. Seppelt has reviewed some aspects of the chemistry of xenon compounds.⁵ A review paper by Andrews⁶ deals with the spectroscopy of the transient XeF in matrixes. The passage of an a.c. electric discharge through binary mixtures of the noble gases and SF₆ produces the monofluorides MF, M = Ar, Kr or Xe, in high yield.⁷ Kuen and Howorka⁸ have commenced an

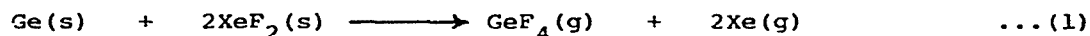
investigation of the properties of rare gas halide ions. The systems studied were Kr(Ar)+Cl₂, Kr(Ar)+CF₄, Kr+SF₆, and Ar+I₂ with mixture ratios varying between 19:1 and 1:10. The ions KrCl⁺, KrF⁺, ArCl⁺ and ArI⁺ were observed but under widely differing reaction conditions, from which the authors have inferred the likely mechanisms of formation.

8.2 XENON(II)

A large number of xenon compounds have been studied⁹ by Mössbauer spectroscopy of ¹²⁹Xe. The quadrupole interaction strengths (Q.S.) of all xenon(II) compounds with linear F-Xe-F groups lie close together, but a small increase of the Q.S. with the acceptor strength of the adduct group was observed. For compounds with F-Xe-O- and -O-Xe-O- groups a reduction of Q.S. was established. Xenon(IV) compounds exhibit a Q.S. similar in magnitude to that of Xe(II) compounds but quite distinct from that of xenon(VI) derivatives.

The collision of electron beams in the energy range 0 to 20eV with XeF₂ molecules results in the production of F⁻, F₂⁻ and XeF⁻.¹⁰ The ion currents due to F₂⁻ and XeF⁻ are 10³ and 10² times smaller than that for F⁻. Traces of XeF₂⁻ and XeF₃⁻ were also detected. The standard heat of formation of XeF₂ has been determined¹¹ by the reaction with solid germanium metal in a calorimetric bomb, equation (1). The value obtained, -163.2 ± 1.3kJ mol⁻¹, agrees well with that, -162.8 ± 0.9kJ mol⁻¹, obtained from the reaction with PF₃.

Bancroft et al.¹² have reported the Xe 3d and 4d shake-up* spectra



of gaseous XeF₂. Using ground state M.O.'s for Xe and XeF₂, Rydberg levels for Xe and XeF₂ from the U.V. spectra, and the Xe gas shake-up spectrum, they have constructed a Xe 3d hole state M.O. diagram for XeF₂. The shake-up peaks have been satisfactorily assigned using this diagram.

* In a shake-up process the energy of the photoelectron leaving the molecule is "shared" with valence electrons and a valence electron is promoted to an excited state.

A volatile, waxy, white solid with a half-life in a Kel-F container of approximately 30min. at room temperature has been obtained by the reaction of XeF_2 with gaseous CF_3 radicals.¹³ The product is believed to be $\text{Xe}(\text{CF}_3)_2$ and has been characterised by F analysis and by i.r. and ^{19}F n.m.r. spectra of partially decomposed samples. Decomposition of the novel compound, the first reported to contain carbon σ bonded to xenon, takes place in Kel-F at 20°C according to equation (2).

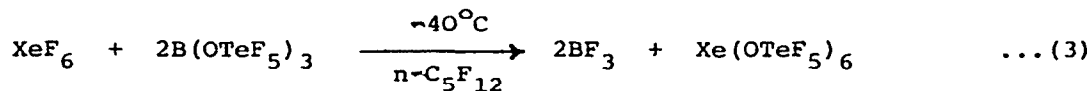


Goncharov and coworkers¹⁴ have calculated the successive one-electron reduction potentials of XeF_2 in aqueous solution on the basis of the available thermodynamic literature data and correlations. They have proposed that the active intermediate involved in oxidation reactions of XeF_2 in aqueous solutions is XeO , on the basis of a study of competitive reactions.¹⁵

The $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -initiated fluorination of norbornene by XeF_2 in dichloromethane produces the novel 2-endo-5-exo- and 2-exo-5-exo-difluoronorbornanes instead of the well known anti- and syn-2,7-difluoronorbornanes.¹⁶ The use of ether as solvent yields the 2,7-difluoro isomers, which are then isomerised to the other pair of isomers by $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Lempert and colleagues¹⁷ have investigated the use of XeF_2 as an oxidant for the determination of Cr^{3+} and Mn^{2+} . Nesmeyanov et al.¹⁸ have reported the fluorination of aryl bromides to the related BrF_2 -derivatives by the action of XeF_2 in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ or HF in CH_2Cl_2 or SO_2 . The yields of these reactive intermediates was claimed to be < 10% at -70°C. Chemical evidence for their formation was provided by the coupling reactions with arenes to give diarylbromonium salts.

8.3 XENON(VI)

Mössbauer studies of ^{129}Xe in xenon(VI) compounds have shown that in this oxidation state the quadrupole interaction strengths (Q.S.) are appreciably different from those of the two lower oxidation states.⁹ In XeF_6 the Q.S. is indicative of appreciable distortion from octahedral coordination: even larger values were found for the adducts and for compounds with mixed O and F ligands. Xenon(VI) fluoride reacts very slowly with $\text{B}(\text{OTeF}_5)_3$ (molar ratio 1:2) according to equation (3).¹⁹ The new xenon(VI) derivative,



$\text{Xe}(\text{OTeF}_5)_6$, precipitates as a red-violet, photosensitive solid; thermal decomposition at -10°C or photolytic (daylight) decomposition, even at -230°C , produces $\text{Xe}(\text{OTeF}_5)_4$ and $\text{F}_5\text{TeOOTeF}_5$. A slow hydrolysis reaction of the compound was also reported; the hydrolysis product was shown to be $\text{OXe}(\text{OTeF}_5)_4$, which was also prepared from the reaction between OXeF_4 and $\text{B}(\text{OTeF}_5)_3$.

The use of XeO_3 as an oxidant in inorganic analysis, for Fe^{2+} and N_2H_4 , has been investigated by Lempert et al.:¹⁷ they also presented kinetic data for the decomposition of XeO_3 . A short-lived molecule or radical, which is a product of the H_2O_2 - XeO_3 reaction, is apparently responsible for the oxidation of Np^{5+} to Np^{6+} in perchloric acid.²⁰

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