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Chapter 8

THE NOBLE GASES

M.F.A.Dove

8.1 THE ELEMENTS

The He-benzene and He_2-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 C_6 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 Bartlett[4] 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 Andrews[6] 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 SF_6 produces the monofluorides MF, M = Ar, Kr or Xe, in high yield.[7] Kuen and Howorka[8] have commenced an investigation of the properties of rare gas halide ions. The systems studied were Kr(Ar)+Cl_2, Kr(Ar)+CF_4, Kr+SF_6, and Ar+I_2 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 studied[9] by Mössbauer spectroscopy of ^{129}Xe. 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 XeF_2 molecules results in the production of F^-, F_2^- and XeF^-.[10] The ion currents due to F_2^- and XeF^- are 10^3 and 10^2 times smaller than that for F^-. Traces of XeF_2^- and XeF_3^- were also detected. The standard heat of formation of XeF_2 has been determined[11] 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 PF_3.

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

$$Ge(s) + 2XeF_2(s) \longrightarrow GeF_4(g) + 2Xe(g) \qquad ...(1)$$

of gaseous XeF_2. Using ground state M.O.'s for Xe and XeF_2, Rydberg levels for Xe and XeF_2 from the U.V. spectra, and the Xe gas shake-up spectrum, they have constructed a Xe 3d hole state M.O. diagram for XeF_2. The shake-up peaks have been satisfactorily assigned using this diagram.

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* 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 $Xe(CF_3)_2$ 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).

$$Xe(CF_3)_2 \longrightarrow XeF_2 + C_nF_m \qquad \ldots(2)$$

Goncharov and coworkers[14] 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 $BF_3.Et_2O$-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 $BF_3.Et_2O$. Lempert and colleagues[17] 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 $BF_3.Et_2O$ 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 lignads. Xenon(VI) fluoride reacts very slowly with $B(OTeF_5)_3$ (molar ratio 1:2) according to equation (3).[19] The new xenon(VI) derivative,

$$XeF_6 + 2B(OTeF_5)_3 \xrightarrow[n\text{-}C_5F_{12}]{-40^{\circ}C} 2BF_3 + Xe(OTeF_5)_6 \quad ...(3)$$

$Xe(OTeF_5)_6$, precipitates as a red-violet, photosensitive solid; thermal decomposition at -10°C or photolytic (daylight) decomposition, even at -230°C, produces $Xe(OTeF_5)_4$ and $F_5TeOOTeF_5$. A slow hydrolysis reaction of the compound was also reported; the hydrolysis product was shown to be $OXe(OTeF_5)_4$, which was also prepared from the reaction between $OXeF_4$ and $B(OTeF_5)_3$.

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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