Coordination Chemistry Reviews, 56 (1984) 471–475
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 8

NOBLE GASES

M.F.A. Dove

8.1 THE ELEMENTS

Although the use of noble gases to provide transparent and inert solid matrices is not reviewed here, it is nevertheless appropriate to draw attention to the more recently developed use of liquified noble gases as solvents. The transparency of such solvents, when pure, towards infrared and visible electromagnetic radiation is an attractive feature. A group of workers at the Los Alamos Scientific Laboratory have reported on the solubility of MoF_6, CO_2, HCHO, HN_3, MeOH, CCl_4, and SO_2 in liquid krypton over the temperature range 118 to 165K.[1] The data at 140K range from 0.1 mol ℓ^{-1} for CO_2 to 2 x 10^{-4} mol ℓ^{-1} for HN_3. Methanol was shown to dissolve as dimers or higher aggregates. The transient near-i.r. absorptions of irradiated noble gases have been studied further: Kasama et al.[2] have assigned them to electronic transitions of the excited diatomic molecules.

The kinetics of the heterogeneous reaction (1) have been reported:[3] from the temperature dependence the effective activation energy was calculated to be 17±2 kcal mol^{-1}. Stein[4]

$$Xe + 2O_2SbF_6 \rightarrow 2O_2 + FXeSb_2F_{11} \qquad ...(1)$$

has described the conditions under which xenon is oxidised by

0010-8545/84/$03.00

elemental fluorine in the dark in the presence of liquid SbF_5. The dixenon cation, Xe_2^+, is formed as a labile intermediate, which is then oxidised by F_2 to XeF^+. The rate of the overall reaction is proportional to the partial pressure of both Xe and F_2. The overall reaction provides a simple method for preparing $XeF^+Sb_2F_{11}^-$.

The transient species resulting from the photodissociation of F_2 in Xe/F_2 and $Xe/Ar/F_2$ mixtures has been monitored by UV kinetic absorption spectroscopy and by laser fluorescence.[5] The calculated heat of formation of XeF(g), 15.5 kcal mol^{-1}, is based upon the measured dissociation energy of ground state XeF (3.4 kcal): hence Messing and Smith deduced that the energy required to remove the first fluorine from XeF_2 is ca. 61 kcal mol^{-1}. This helped them to understand that reaction (2) appears to be

$$XeF + F_2 \rightarrow XeF_2 + F \qquad ...(2)$$

$$XeF + XeF \rightarrow XeF_2 + Xe \qquad ...(3)$$

the main process by which XeF is converted to XeF_2 in their systems at low pressures. At higher pressures reaction (3) may also be important.

8.2 KRYPTON(II) AND XENON(II)

Spitzin et al.[6] have described the synthesis of LnF_4 (Ln = Ce, Pr and Tb) and Cs_3LnF_7 (Ln = Ce, Tb, Pr, Dy and Nd) by fluorination reactions involving noble gas fluorides. Thus PrF_4 could be prepared only by the reaction of KrF_2 with PrO_2.

An X-ray crystallographic study of fluoro[imidobis(sulphuryl fluoride)]xenon(II), $FXeN(SO_2F)_2$, has provided definitive proof that this molecule indeed contains, see Figure 1, a Xe-N and a Xe-F bond which are essentially colinear, FXeN angle 178.1°, at -55°C.[7] The ^{15}N and ^{129}Xe n.m.r. study of the compound in solution in BrF_5 has provided fuller proof that the structure in solution is the same. A new system containing Xe(II) bonded to N has been reported:[8] it is derived from the recently prepared $(CF_3SO_2)_2NH$ by the reaction with XeF_2. A cleaner reaction was obtained via the trimethylsilylimide intermediate $(CF_3SO_2)_2NSiMe_3$. This reacts with XeF_2 according to equation (4) in high yield. The novel compound is a solid, stable under N_2 or in vacuo at 22°C

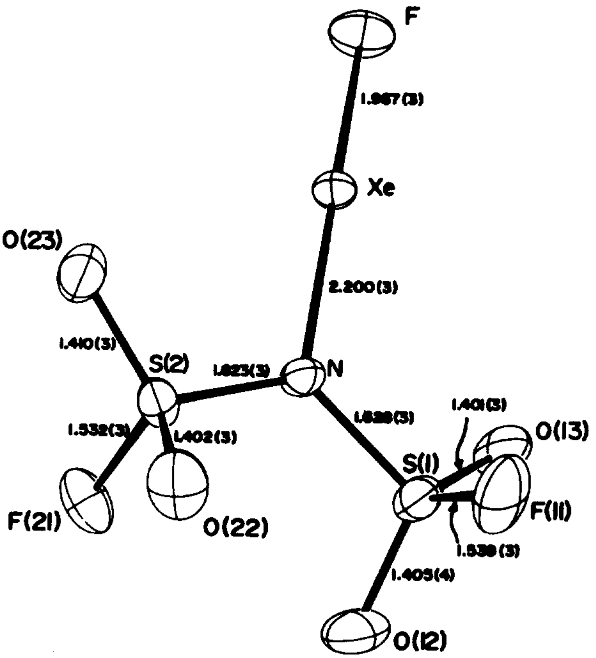

Figure 1. A perspective drawing of $FXeN(SO_2F)_2$ showing the bond lengths (Å) and thermal ellipsoids drawn at the 50% probability level (reproduced by permission from Inorg. Chem., 21(1982)4065).

for several days. It decomposes at 72°C to give Xe, C_2F_6,

$$2Me_3SiN(SO_2CF_3)_2 + XeF_2 \rightarrow Xe(N(SO_2CF_3)_2)_2 + 2Me_3SiF \qquad ...(4)$$

$(CF_3SO_2)_2NCF_3$, and $CF_3SO_2NSO_2$. There was no evidence for the formation of $(CF_3SO_2)_2NXeF$ in any of these reactions. Huston[9] has investigated the ammonolysis of XeF_2 and detected Xe, N_2, HF and ammonium fluoride.

8.3 XENON(IV)

Xenon(IV) fluoride reacts with NH_3 similarly but forms XeF_2 as an intermediate product.[9] The hydrolysis of XeF_4 has also been reinvestigated by Huston.

8.4 XENON(VI)

Xenon(VI) fluoride yields a range of ammonolysis products; with excess ammonia the products are the same as those yielded by XeF_2 and XeF_4.[9] However with excess XeF_6 an explosive white solid was reported, for which some formulations were proposed. A more controlled hydrolysis of XeF_6 has been achieved by the reaction with $HOPOF_2$.[10] Yellow NF_4XeF_7 and white $(NF_4)_2XeF_8$ have been prepared from XeF_6 and NF_4HF_2 and by reaction (5), respectively.[11] Even the XeF_7^- salt was shown to undergo solvolysis in BrF_5. The

$$2NF_4XeF_7 \xrightarrow[R.T.]{488nm} (NF_4)_2XeF_8 + XeF_6 \qquad ...(5)$$

presence of different phases in solid XeF_6 was confirmed by Christe and Wilson[11] by Raman spectroscopy. They also prepared $CsXeF_7$, Cs_2XeF_8 and $NaXeF_7$.

Pulse radiolysis of aqueous XeO_3 and $HXeO_4^-$ has been shown to produce Xe(V) and Xe(VII) species respectively.[12] The hydrated electron converts XeO_3 to $HXeO_3$ and the hydroxyl radical converts it to $HOOXeO_2$.

8.5 XENON(VIII)

An improved synthesis of perxenates has been published by Foropoulos and DesMarteau[10] in which the XeF_6 is hydrolysed initially by $HOPOF_2$; subsequent hydrolysis of XeO_3 gave pure Na_4XeO_6 in high yield.

Pulse radiolysis of Xe(VIII) yields evidence for Xe(VII) and Xe(IX) depending on the reaction conditions.[12]

Huston[9] has reported the melting point of XeO_4 ($-35.9^{o}C$) and of XeO_3F_2 ($-54.1^{o}C$) as well as some vapour pressure measurements for the latter.

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