

## Chapter 8

### NOBLE GASES

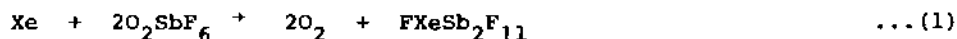
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#### 8.1 THE ELEMENTS

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  $\text{MoF}_6$ ,  $\text{CO}_2$ ,  $\text{HCHO}$ ,  $\text{HN}_3$ ,  $\text{MeOH}$ ,  $\text{CCl}_4$ , and  $\text{SO}_2$  in liquid krypton over the temperature range 118 to 165K.<sup>1</sup> The data at 140K range from 0.1 mol  $\ell^{-1}$  for  $\text{CO}_2$  to  $2 \times 10^{-4}$  mol  $\ell^{-1}$  for  $\text{HN}_3$ . 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.<sup>2</sup> have assigned them to electronic transitions of the excited diatomic molecules.

The kinetics of the heterogeneous reaction (1) have been reported:<sup>3</sup> from the temperature dependence the effective activation energy was calculated to be  $17 \pm 2$  kcal mol<sup>-1</sup>. Stein<sup>4</sup>



has described the conditions under which xenon is oxidised by

elemental fluorine in the dark in the presence of liquid  $\text{SbF}_5$ . The dioxenon cation,  $\text{Xe}_2^+$ , is formed as a labile intermediate, which is then oxidised by  $\text{F}_2$  to  $\text{XeF}^+$ . The rate of the overall reaction is proportional to the partial pressure of both Xe and  $\text{F}_2$ . The overall reaction provides a simple method for preparing  $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ .

The transient species resulting from the photodissociation of  $\text{F}_2$  in  $\text{Xe}/\text{F}_2$  and  $\text{Xe}/\text{Ar}/\text{F}_2$  mixtures has been monitored by UV kinetic absorption spectroscopy and by laser fluorescence.<sup>5</sup> The calculated heat of formation of  $\text{XeF}(\text{g})$ ,  $15.5 \text{ kcal mol}^{-1}$ , is based upon the measured dissociation energy of ground state  $\text{XeF}$  (3.4 kcal): hence Messing and Smith deduced that the energy required to remove the first fluorine from  $\text{XeF}_2$  is ca.  $61 \text{ kcal mol}^{-1}$ . This helped them to understand that reaction (2) appears to be

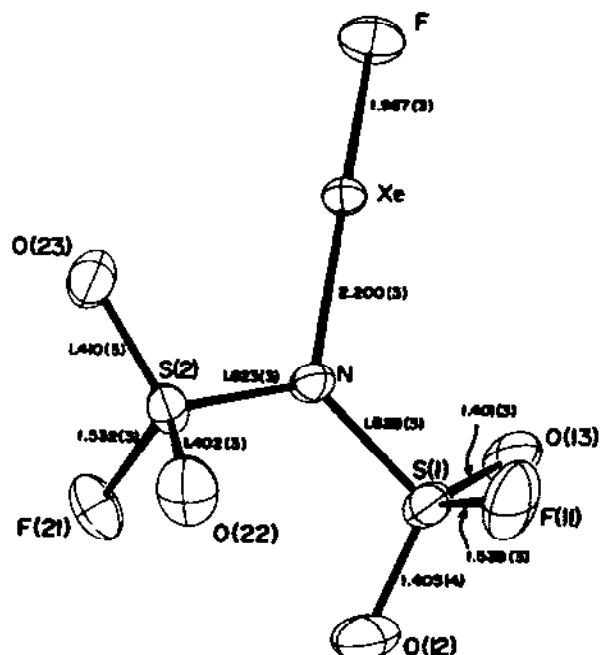


the main process by which  $\text{XeF}$  is converted to  $\text{XeF}_2$  in their systems at low pressures. At higher pressures reaction (3) may also be important.

## 8.2 KRYPTON(II) AND XENON(II)

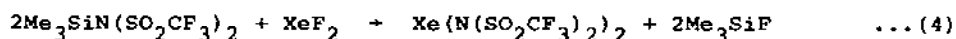
Spitzin et al.<sup>6</sup> have described the synthesis of  $\text{LnF}_4$  ( $\text{Ln} = \text{Ce}$ ,  $\text{Pr}$  and  $\text{Tb}$ ) and  $\text{Ca}_3\text{LnF}_7$  ( $\text{Ln} = \text{Ce}$ ,  $\text{Tb}$ ,  $\text{Pr}$ ,  $\text{Dy}$  and  $\text{Nd}$ ) by fluorination reactions involving noble gas fluorides. Thus  $\text{PrF}_4$  could be prepared only by the reaction of  $\text{KrF}_2$  with  $\text{PrO}_2$ .

An X-ray crystallographic study of fluoro[imidobis(sulphuryl fluoride)]xenon(II),  $\text{FXeN}(\text{SO}_2\text{F})_2$ , has provided definitive proof that this molecule indeed contains, see Figure 1, a Xe-N and a Xe-F bond which are essentially colinear,  $\text{FXeN}$  angle  $178.1^\circ$ , at  $-55^\circ\text{C}$ .<sup>7</sup> The  $^{15}\text{N}$  and  $^{129}\text{Xe}$  n.m.r. study of the compound in solution in  $\text{BrF}_5$  has provided fuller proof that the structure in solution is the same. A new system containing  $\text{Xe}(\text{II})$  bonded to N has been reported:<sup>8</sup> it is derived from the recently prepared  $(\text{CF}_3\text{SO}_2)_2\text{NH}$  by the reaction with  $\text{XeF}_2$ . A cleaner reaction was obtained via the trimethylsilylimide intermediate  $(\text{CF}_3\text{SO}_2)_2\text{NSiMe}_3$ . This reacts with  $\text{XeF}_2$  according to equation (4) in high yield. The novel compound is a solid, stable under  $\text{N}_2$  or in vacuo at  $22^\circ\text{C}$



**Figure 1.** A perspective drawing of  $\text{FxeN}(\text{SO}_2\text{F})_2$  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  $72^\circ\text{C}$  to give Xe,  $\text{C}_2\text{F}_6$ ,



$(\text{CF}_3\text{SO}_2)_2\text{NCF}_3$ , and  $\text{CF}_3\text{SO}_2\text{NSO}_2$ . There was no evidence for the formation of  $(\text{CF}_3\text{SO}_2)_2\text{NXeF}$  in any of these reactions. Huston<sup>9</sup> has investigated the ammonolysis of  $\text{XeF}_2$  and detected Xe,  $\text{N}_2$ , HF and ammonium fluoride.

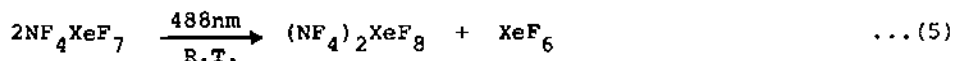
### 8.3 XENON(IV)

Xenon(IV) fluoride reacts with  $\text{NH}_3$  similarly but forms  $\text{XeF}_2$  as an intermediate product.<sup>9</sup> The hydrolysis of  $\text{XeF}_4$  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  $\text{XeF}_2$  and  $\text{XeF}_4$ .<sup>9</sup> However with excess  $\text{XeF}_6$  an explosive white solid was reported, for which some formulations were proposed. A more controlled hydrolysis of  $\text{XeF}_6$  has been achieved by the reaction with  $\text{HOPOF}_2$ .<sup>10</sup> Yellow  $\text{NF}_4\text{XeF}_7$  and white  $(\text{NF}_4)_2\text{XeF}_8$  have been prepared from  $\text{XeF}_6$  and  $\text{NF}_4\text{HF}_2$  and by reaction (5), respectively.<sup>11</sup> Even the  $\text{XeF}_7^-$  salt was shown to undergo solvolysis in  $\text{BrF}_5$ . The



presence of different phases in solid  $\text{XeF}_6$  was confirmed by Christe and Wilson<sup>11</sup> by Raman spectroscopy. They also prepared  $\text{CsXeF}_7$ ,  $\text{Cs}_2\text{XeF}_8$  and  $\text{NaXeF}_7$ .

Pulse radiolysis of aqueous  $\text{XeO}_3$  and  $\text{HXeO}_4^-$  has been shown to produce  $\text{Xe(V)}$  and  $\text{Xe(VII)}$  species respectively.<sup>12</sup> The hydrated electron converts  $\text{XeO}_3$  to  $\text{HXeO}_3$  and the hydroxyl radical converts it to  $\text{HOOXeO}_2$ .

### 8.5 XENON(VIII)

An improved synthesis of perxenates has been published by Foropoulos and DesMarteau<sup>10</sup> in which the  $\text{XeF}_6$  is hydrolysed initially by  $\text{HOPOF}_2$ ; subsequent hydrolysis of  $\text{XeO}_3$  gave pure  $\text{Na}_4\text{XeO}_6$  in high yield.

Pulse radiolysis of  $\text{Xe(VIII)}$  yields evidence for  $\text{Xe(VII)}$  and  $\text{Xe(IX)}$  depending on the reaction conditions.<sup>12</sup>

Huston<sup>9</sup> has reported the melting point of  $\text{XeO}_4$  ( $-35.9^\circ\text{C}$ ) and of  $\text{XeO}_3\text{F}_2$  ( $-54.1^\circ\text{C}$ ) as well as some vapour pressure measurements for the latter.

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