Schrobilgen

Note Title 4/5/2005

Bartlett - 1962

studying powerful oxidants

PtF_6 + Xe

I.p. of O_2 similar to Xe...

initial formulation: $Xe^+ PtF_6^-$

reformulation: XeF^+

Website: pubs.acs.org/cen/80th/noblegases.html

Gillespie
- Canadian
- noble gas chemistry
- VSEPR - ELF

XeF_2 as fluorinating agent

delivery of ^{18}F - positron emitter (PET)

L-DOPA ^{18}F synthesis

^{129}Xe NMR to probe gas-accessible chambers

	ΔH_f° (kJ/mol)
XeF_2	−162.8
XeF_4	−267.1
XeF_6	−338.2
KrF_2	+60.2 ↑ endothermic

most well known krypton compound

① particle beam
② electric discharge
③ UV- irradiation
④ hot wire

} atomize the fluorine

$$Kr/F_2 \xrightarrow[20\,K]{h\nu} F-Kr-F$$

580 cm^{-1} ν_3 Σ_u^+
236 cm^{-1} ν_2 Π_u

F_2 activation at low T:

$F_2 \longrightarrow 2\ F\cdot$

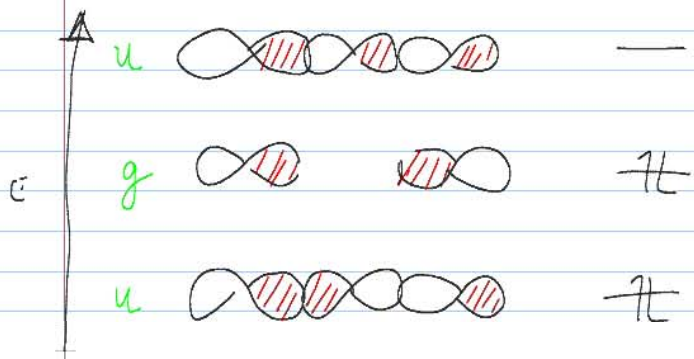
$F\cdot + Kr \text{—} (\cdot KrF)$ observed

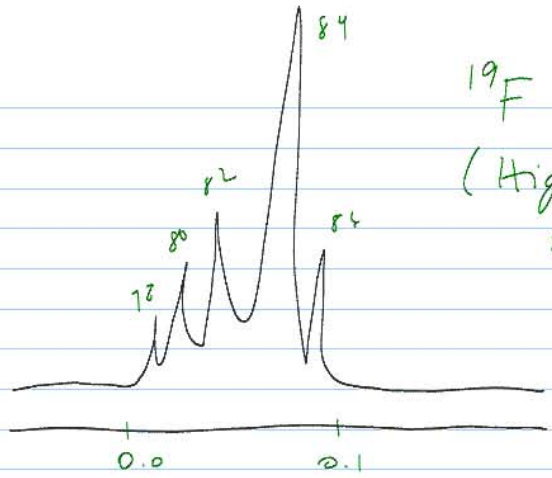
$2\ \cdot KrF \longrightarrow F\text{–}Kr\text{–}F + Kr$

$\cdot KF + \cdot F \longrightarrow F\text{–}Kr\text{–}F$

Bonding in KrF_2

Bond order = 0.5





^{19}F NMR of KrF_2
(High-res)

^{83}Kr n.a. 11%
$I = 9/2$

"Isotopic Perturbation of Resonance" IPR

reacts explosively with organics and H_2O!

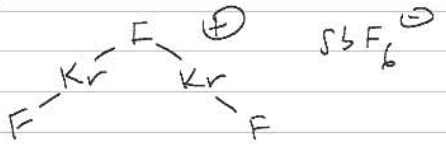
KrF_2 solvents: SO_2ClF, BrF_5, HF

$$7\,KrF_2 + 2\,Au \xrightarrow{HF} 2\,KrF^{\oplus}\,AuF_6^{\ominus} + 5\,Kr\uparrow$$

important as a heat sink.

$$KrF_2 + 2\,SbF_5 \longrightarrow KrF^{\oplus}\ F{-}Sb(F)_4{-}F{-}Sb(F)_4{-}F^{\ominus}$$

$$2\,KrF_2 + SbF_5 \longrightarrow$$



Kr – E bonds (E = N, O, C)

$HCN-KrF^{\oplus}\ AsF_6^{\ominus} + HF$

↑ HF (not HCN!)

$HCNH^{\oplus}\ AsF_6^{\ominus} + KrF_2$

$3\ KrF_2 + 2\ B(OTeF_5)_3 \longrightarrow 3$

"Teflate"

$Kr(OTeF_5)_2 + 2\ BF_3$

-78 ↓

$Kr + F_5TeOOTeF_5$

Xe analog stable to +160 °C!