Krypton Fluoride Chemistry; a Route to AuF_5, $KrF^+AuF_6^-$, $Xe_2F_3^+AuF_6^-$, and $NO^+AuF_6^-$: The KrF^+–$XeOF_4$ System

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Summary Pyrolysis of newly prepared $KrF^+AuF_6^-$ gives AuF_5 which reacts with XeF_2 to produce $Xe_2F_3^+AuF_6^-$ and NOF to give $NO^+AuF_6^-$; $Kr^+AuF_6^-$ is a powerful oxidative fluorinating agent with respect to O_2 and Xe and the reaction of KrF^+ with excess $XeOF_4$ gives $XeOF_4.XeF_5^+$ and O_2^+ salts, not $XeOF_5^+$ as reported previously.

KRYPTON DIFLUORIDE, KrF^+, and $Kr_2F_3^+$ are all powerful oxidative fluorinating agents. Oxidation of xenon to XeF_6, iodine to IF_7,[1] O_2 to O_2^+, Xe to XeF_5^+[2,3] and BrF_5 to BrF_6^+[2,4] are all possible with these reagents at low temperature. The last reaction, using krypton fluoride cations, is significant since it has provided the first synthesis of BrF_6^+ when other methods, including the use of powerful oxidants like PtF_6 have failed. We now report the use of krypton fluoride cations for the synthesis of a number of previously unreported Au^V species, and also show that the results of the reaction of KrF^+ salts with $XeOF_4$ have previously been misinterpreted.

When KrF_2 was treated with Au powder in HF the

$$7KrF_2 + 2Au \xrightarrow{20\,°C} 2KrF^+AuF_6^- + 5Kr \qquad (1)$$

resulting product was a light yellow solid which was sparingly soluble in HF to give a pale yellow solution (equation 1). Excess KrF_2 and HF solvent were removed by rapid pumping at 0 °C. The Raman spectrum of the powder, recorded at −80 °C under a layer of HF, is consistent with a formulation in which the KrF^+ cation is fluorine-bridged to the AuF_6^- anion;† ν(Kr–F) 597(82), ν(Kr---F) 346(2), and δ(F–Kr---F) 163(2) cm^{-1}. Lines attributable to a distorted AuF_6^- anion were observed at $\nu_8(e)$ 650(34), $\nu_1(a_1)$ 603(100), $\nu_2(a_1)$ 541(sh), $\nu_5(b_1)$ 530(19), $\nu_4(a_1)$ 471(1), $\nu_7(b_2)$ 278(2), $\nu_3(a_1)$ 233(11), $\nu_9(e)$ 226(17), and $\nu_{11}(e)$ 219(12) and are

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† All the krypton and xenon adducts reported are represented in terms of ionic formulations. Since these molecules have significant covalent contributions to their bonding in the form of fluorine bridging, it is stressed that the ionic representations are strictly a formalism (*cf.* refs. 1—4).

assigned on the basis of approximate C_{4v} symmetry for the anion.[3]

$KrF^+AuF_6^-$ is an extremely potent oxidative fluorinating agent. It reacts rapidly at room temperature with oxygen gas to yield $O_2^+AuF_6^-$. The observed Raman frequencies are $\nu(O_2^+)$ 1836(63); AuF_6^-, $\nu_1(a_{1g})$ 598(100), $\nu_2(e_g)$ too weak to be observed, and $\nu_3(t_{2g})$ 230(33) [*cf.* $Cs^+AuF_6^-$, $\nu_1(a_{1g})$ 595(66), $\nu_2(e_g)$ 520(28) and $\nu_5(t_{2g})$ 224(25) in ref. 5]. The reaction with xenon at room temperature is more complex. An HF solution of the dark red-orange product yields a bright yellow solution which was shown by ^{19}F n.m.r. spectroscopy to contain the XeF_5^+ cation (identified by its AX_4 spectrum and accompanying ^{129}Xe satellites[6] and AuF_6^- (shown by a sharp singlet at 117·0 p.p.m.) as well as an insoluble yellow-brown solid which has not been characterised. Complete collapse of the ^{197}Au–^{19}F spin–spin coupling in AuF_6^- (^{197}Au 100%, I $^3/_2$) indicates that the electric field gradient at gold is not spherical in HF solvent.

Pyrolysis of $KrF^+AuF_6^-$ at 60—65 °C yields pure AuF_5 according to equation (2).

$$KrF^+AuF_6^- \xrightarrow[8\ \mathrm{h}]{60\text{—}65\ ^\circ\mathrm{C}} AuF_5 + Kr + F_2 \qquad (2)$$

The empirical formula $AuF_{4\cdot98}$, deduced from the elemental analyses, is in excellent agreement with the proposed pentafluoride formulation. AuF_5 is dark red-brown when massive, but orange when powdered. *X*-ray powder photographs show that no AuF_3 is present in any of our AuF_5 preparations and indicates that AuF_5 is distinctly different from the monoclinic, MoF_5-type[7] and orthorhombic, ReF_5-type structures.[7] Similarities to the monoclinic, RuF_5-type patterns, however, suggest that AuF_5 may also be tetrameric containing bent Au---F---Au bridge bonds. Three bands were observed in the room-temperature Raman spectrum of solid AuF_5 at 658(43), 598(100) and 228(25) cm^{-1}.

The direct interaction of excess XeF_2 with AuF_5 in HF or BrF_5 gave $Xe_2F_3^+AuF_6^-$ on removal of solvent and excess XeF_2 under vacuum. In addition to lines assignable to the $Xe_2F_3^+$ cation, the Raman spectrum of the pale-yellow solid contained lines which can be readily assigned to the AuF_6^- anion at $\nu_1(a_{1g})$ 597(64), 594(100); $\nu_2(e_g)$ 528(12); and $\nu_5(t_{2g})$ 222(17) cm^{-1}. $NO^+AuF_6^-$ was prepared by the interaction of excess NOF and AuF_5 in HF. Removal of excess NOF and HF under vacuum gave a pale yellow solid whose Raman spectrum was consistent with the proposed formulation: $\nu(NO^+)$ 2329(2); $\nu_1(a_{1g})$ 603(100), 600(99); $\nu_2(e_g)$ too weak to be observed, and $\nu_5(t_{2g})$ 236(16), 231(16). The i.r. spectrum was poorly defined except for a sharp peak at 2330 cm^{-1} assigned to $\nu(NO^+)$.

Bartlett and his co-workers[8] have previously reported that the reaction of $KrF^+Sb_2F_{11}^-$ with $XeOF_4$ in a silica reaction vessel gives rise to the $XeOF_5^+$ cation as well as O_2^+. The origin of O_2^+ was attributed to the reaction of KrF^+ with the reaction vessel. We have now re-investigated this system in FEP containers. The reaction of excess $XeOF_4$ with $KrF^+SbF_6^-$ or $KrF^+Sb_2F_{11}^-$ yields a white solid when excess $XeOF_4$ is removed under vacuum at 20 °C. Using $KrF^+SbF_6^-$ the Raman spectrum was identical with that reported previously by Bartlett *et al.* for $XeOF_5^+\ Sb_nF_{5n-1}^-$ while using $KrF^+Sb_2F_{11}^-$ the same spectrum was obtained, but it also contained lines assignable to $O_2^+SbF_6^-$[9] and $XeOF_3^+SbF_6^-$.[10] The room temperature ^{19}F n.m.r. spectrum of the former solid was examined in HF solution and was shown to consist of a singlet with ^{129}Xe satellites [$-92\cdot1$ p.p.m., $J(^{129}Xe–^{19}F)$ 1154 Hz] and an AX_4 spectrum with ^{129}Xe satellites [F_A $-227\cdot7$ and F_X $-106\cdot8$ p.p.m., $J(^{129}Xe–^{19}F_A)$ 1390, $J(^{129}Xe–^{19}F_X)$ 177, and J_{FF} 179 Hz]. The integrated relative intensities of the singlet and its satellites and the X_4 part of the AX_4 spectrum and its satellites were 1:1. The ^{19}F n.m.r. results are consistent with a 1:1 molar mixture of $XeOF_4$[11] and XeF_5^+[6] in solution. Cooling of the sample to -80 °C in the n.m.r. probe resulted in a white precipitate and a corresponding dimunition of the $XeOF_4$ and XeF_5^+ ^{19}F n.m.r. intensities. The Raman spectrum of the precipitate was recorded ***in situ*** at –80 °C and shown to be identical with that observed for the solid prior to solution in HF. The Raman spectrum of the solid can therefore be assigned in terms of the molecular adduct $XeOF_4.XeF_5^+SbF_6^-$. XeF_5^+ [$\nu_1(a_1)$ 675(3); $\nu_2(a_1)$ 618(100); $\nu_4(b_1)$ 561(16); $\nu_8(e)$ 409(8); $\nu_3(a_1)$ 364(sh); $\nu_6(b_2)$ 313(4), 304(sh), *cf.* ref. 12], $SbF_6^-(C_{4v})$ [$\nu_8(e)$ 698(2), 690(50); $\nu_1(a_1)$ 664(6); $\nu_2(a_1)$ 654(10); $\nu_4(a_1)$ 444(1); $\nu_9(e)$ 284(2); $\nu_3(a_1)$ 278(4); $\nu_{11}(e)$ 256(0·5), *cf.* ref. 3], $XeOF_4$ [$\nu_1(a_1)$ 921(24); $\nu_2(a_1)$ 576(68); $\nu_5(b_2)$ 542(69); $\nu_8(e)$ 372(10); $\nu_3(a_1)$ 295(9); $\nu_4(b_1)$ 235(6); $\nu^9(e)$ 166(1), 158(2), *cf.* ref. 13].

The reactions of KrF^+ salts with excess $XeOF_4$ presumably occur according to equations (3) and (4) and do not

$$KrF^+ + 2XeOF_4 \rightarrow XeOF_4.XeF_5^+ + Kr + \tfrac{1}{2}O_2 \qquad (3)$$

$$O_2 + KrF^+ \rightarrow O_2^+ + Kr + \tfrac{1}{2}F_2 \qquad (4)$$

yield $XeOF_5^+$ as previously reported.[8]

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