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COVALENT XENON DERIVATIVES OF THE OXYTETRAFLUOROIODINEOXIDE GROUP, $O{=}IF_4O-$

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With improved synthetic procedures for the precursor iodine (VII) oxyfluoride, $(IO_2F_3)_2$, significant chemistry for the $O{=}IF_4O-$ group is beginning to emerge. In the present work, the covalent xenon(II) species $FXeOIOF_4$ and $Xe(OIOF_4)_2$ (including all isomers derived from cis-trans isomerism associated with the $O{=}IF_4O-$ group) have been observed in solution mixtures of IO_2F_3 and XeF_2 by high-field ^{19}F (235 MHz) and ^{129}Xe NMR spectroscopy. The net insertion of IO_2F_3 into the Xe-F bonds of XeF_4 and $O{=}XeF_4$ has also been observed to give rise to the Xe(IV) and Xe(VI) derivatives $F_3XeOIOF_4$ and $O{=}XeF_3(OIOF_4)$. The reaction of XeF_6 with $(IO_2F_3)_2$ has yielded the ionic compound, $XeF_5^+IO_2F_4^-$. 129-Xenon chemical shift trends among the F_5TeO-, $O{=}IF_4O-$ and F-analogs of the aforementioned derivatives have been used to establish that the $O{=}IF_4O-$ group is more electronegative than the F_5TeO-group.

Generally, it has not proven possible to isolate $O{=}IF_4O-$ derivatives by routes analogous to those used in the syntheses of F_5TeO- derivatives. Both cis,cis-$Xe(OIOF_4)_2$ and a mixture of cis- and trans-$FXeOIOF_4$ have been isolated and characterized by low-temperature Raman spectroscopy. The former is a pale yellow solid that is stable at 0°C and generated upon displacement of $HOTeF_5$ with the stronger acid $HOIOF_4$ while $FXeOIOF_4$ is formed in the stoichiometric reaction of XeF_2 and $Xe(OIOF_4)_2$. $FXeOIOF_4$ melts at 0 to 5°C to give a pale yellow liquid which is stable for up to several hours at room temperature. The cis,cis-$Hg(OIOF_4)_2$ derivative has also been prepared by the same method and similarly characterized. An analogous series of $O{=}Xe(OTeF_5)_{4-x}(OIOF_4)_x$ derivatives have been generated in successive acid displacements involving $HOIOF_4$ and $O{=}Xe(OTeF_5)_4$ and studied by ^{129}Xe NMR spectroscopy.

The bis-xenon(II) derivatives have been shown to be unstable above 0°C. Controlled pyrolysis of solid cis,cis-$Xe(OIOF_4)_2$ has been utilized to prepare the corresponding peroxide, $O{=}IF_4{-}O{-}O{-}F_4I{=}O$. The latter is stable at room temperature and has been characterized by both low-temperature Raman and high-field ^{19}F NMR spectroscopy.