

The reactivity of the electrophilic cation $[\text{C}_6\text{F}_5\text{Xe}]^+$

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The reactivity of electrophilic cations is principally influenced by the counter anion and additionally in solution by interactions with solvent molecules and depends strongly on the temperature. The influence of different types of solvents (MeCN and AHF) on the properties of the electrophilic cation $[\text{C}_6\text{F}_5\text{Xe}]^+$ and its reactivity are presented; inter alia these influences are discussed for the reaction of $[\text{C}_6\text{F}_5\text{Xe}]^+$ with simple anionic nucleophiles such as halide ions.

In the basic solvent MeCN [1], as well as in the acidic solvent AHF, the soft nucleophile I^- reacts spontaneously with formation of $\text{C}_6\text{F}_5\text{I}$. With the harder nucleophiles Cl^- and especially F^- , a different type of product is obtained and the reactivity of $[\text{C}_6\text{F}_5\text{Xe}]^+$ depends strongly on the solvent. In AHF to 20 °C Cl^- and F^- undergo no reaction with the electrophilic cation, whereas in MeCN at low temperature the coordination sphere of $[\text{C}_6\text{F}_5\text{Xe}]^+$ is changed. The binuclear fluoride-bridged cation $[\text{C}_6\text{F}_5\text{Xe} \cdots \text{F} \cdots \text{XeC}_6\text{F}_5]^+$ is obtained as the low-temperature reaction product in the heterogeneous reaction with CsF . In addition to NMR characterization (^{19}F , ^{13}C and ^{129}Xe), various reactions provide evidence for this new type of arylxenonium cation. Thus with Lewis acids, $[\text{C}_6\text{F}_5\text{Xe}]^+$ is again formed and on heating the binuclear cation in MeCN solution equal amounts of the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation and the $\text{C}_6\text{F}_5\cdot$ radical are formed. The latter is converted predominantly to $\text{C}_6\text{F}_5\text{H}$ or $\text{C}_6\text{F}_5\text{D}$, depending on the solvent, and to $\text{C}_6\text{F}_5\text{C}_6\text{F}_5$. The binuclear cation is isoelectronic with the $[(\text{C}_6\text{F}_5)_2\text{I}]^+$ anion reported by Farnham et al. [2], but the bridging fluoride ion shows a ^{19}F NMR resonance at higher frequency.

Comparison of the structural and spectroscopic features and reactivity patterns of $[\text{C}_6\text{F}_5\text{Xe}]^+$ with those of $[(\text{C}_6\text{F}_5)_2\text{I}]^+$ shows a fundamental relationship between both onium ions and helps in understanding the

bonding of the bridging fluoride ion. From ^{19}F NMR measurements it is deduced that $[(\text{C}_6\text{F}_5)_2\text{I}]^+$ in MeCN is coordinated by the basic solvent in the presence of weak nucleophilic anions such as $[\text{BF}_4]^-$ or $[\text{AsF}_6]^-$, whereas stronger nucleophilic anions such as Cl^- or F^- interact strongly with the electrophilic I^{III} centre. Thus ^{19}F NMR spectroscopy of $[(\text{C}_6\text{F}_5)_2\text{I}]\text{F}$ shows a resonance in MeCN (–13.4 ppm) as well as in CH_2Cl_2 (–12.6 ppm) corresponding to the iodine-bonded fluorine at a frequency comparable to that of the binuclear arylxenonium cation. The solid-state structure of the related compound $[(\text{C}_6\text{F}_5)_2\text{IF}]_2 \cdot [(\text{C}_6\text{F}_5)_2(2,4\text{-C}_6\text{H}_3\text{F}_2)\text{-IF}]_2$ displays an eight-membered I–F ring with I–F distances of 2.362 Å and 2.440 Å, respectively. The coordination of I^{III} is square planar and both C–I bonds on I^{III} are lengthened compared with those in diaryliodonium cations. Finally, the fluoride bridge in the binuclear arylxenonium cation should differ significantly from the short fluorine bridge in $[\text{Xe}_2\text{F}_3]^+$ and should be of comparable length to those in the neutral $[\text{R}_2\text{I}]\text{F}$ compounds or the anion $[(\text{C}_6\text{F}_5)_2\text{F}]^-$.

The solvent also influences the chemistry in parts of the molecule other than the electrophilic centre – which is xenon(II) in this case. This explains the reaction of $[\text{C}_6\text{F}_5\text{Xe}]^+$ with XeF_2 in AHF, where the aryl group is fluorinated without breaking the xenon–carbon bond [3].

The same concept which has allowed us to realize the regiospecific fluorination of $\text{C}_6\text{F}_5\text{I}$ to heptafluoro-1-iodo-1,4-cyclohexadiene using IF_5 in the presence of BF_3 has been employed for the regiospecific fluorination of the isoelectronic species $[\text{C}_6\text{F}_5\text{Xe}]^+$ with XeF_2 in the presence of the Lewis acid solvent AHF. Thus the new alkenylxenonium cations (heptafluoro-1,4-cyclohexadien-1-yl) xenon and (nonafluorocyclohexen-1-yl) xenon can be isolated in a stepwise fashion. In the presence of stoichiometric amounts of water, it is also possible to synthesize the (pentafluoro-3-oxo-1,4-cyclohexadienyl) xenon(II) cation.

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Initial examples which demonstrate the reactivity of the new alkenylxenonium cations with different types of nucleophiles are discussed.

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References

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