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On fluoro-organo tellurium, iodine and xenon derivatives

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Abstract

The syntheses, thermal and chemical stabilities as well as the reactivities of an isovalent series of CF_3 and C_6F_5 compounds of Te, I and Xe have been compared.

In the isovalent series $Te(CF_3)_2$, ICF_3 and Xe, an increase in stability is observed from the Te compound to elemental xenon. $Te(CF_3)_2$ and ICF_3 can be prepared via thermal reactions from $Hg(CF_3)_2$ and $TeCl_4$ and I_2, respectively. A variation in stability is observed in oxidation reactions. Xenon is only oxidized by elemental fluorine, ozone is required for the oxidation of ICF_3, while elemental oxygen suffices for the oxidation of $Te(CF_3)_2$. This variation raises the question as to whether the neutral compounds $Te(CF_3)_4$, $I(CF_3)_3$ and $Xe(CF_3)_2$ or the cations $[Te(CF_3)_3]^+$, $[I(CF_3)_2]^+$ and $[XeCF_3]^+$ exist.

Keywords: Fluoro-organotellurum derivatives; Fluoro-organo iodine derivatives; Fluoro-organo xenon derivatives; Syntheses; Thermal stability; Chemical stability

$Te(CF_3)_4$ can be prepared as a 1:1 adduct with Lewis bases from the reaction of $(CF_3)_2TeCl_2$ with $Cd(CF_3)_2$ complexes at low temperature [1]. At ca. 0 °C it decomposes by the loss of 2 equiv. of CF_2 to give $(CF_3)_2TeF_2$. Only poor NMR spectroscopic evidence has been found for the existence of $I(CF_3)_3$. The primary products of the low-temperature exchange reactions of CF_3IX_2 ($X = Cl, OCOCF_3$) with $Cd(CF_3)_2 \cdot D$ are CF_3IF_2, C_2F_6, ICF_3, $CClF_3$ (from CF_3ICl_2) together with consecutive CF_2 products [2]. Whether $Xe(CF_3)_2$ exists remains controversial to this day.

In contrast to $Te(CF_3)_4$, the salt $[Te(CF_3)_3]^+[BF_4]^-$ is remarkably stable with a melting point of +85 °C. $[Te(CF_3)_3]^+$ is isoelectronic with $Sb(CF_3)_3$ and this fact may explain the stability of the salt up to 300 °C. The $[I(CF_3)_2]^+$ cation is detected in reaction mixtures of CF_3IX_2 and $Cd(CF_3)_2 \cdot 2CH_3CN$ in the presence of a Lewis acid at temperatures up to −20 °C. These comparisons lead to the conclusion that the chances for the synthesis of $Xe(CF_3)_2$ are very low and only a little higher for compounds containing the $[XeCF_3]^+$ cation.

The same arguments can also be applied to the C_6F_5 derivatives. $Te(C_6F_5)_4$ is a stable solid which decomposes at 200 °C to give $Te(C_6F_5)_2$ and $(C_6F_5)_2$ [3]. $I(C_6F_5)_3 \cdot CH_3CN$, which may be prepared from $C_6F_5IF_2$ and $(CH_3)_3SiC_6F_5$, eliminates $(C_6F_5)_2$ even at room temperature. Consequently, decomposition of the as yet unknown $Xe(C_6F_5)_2$ should be appreciable even below room temperature.

The $[XeC_6F_5]^+$ cation is definitely stable to higher than 0 °C. Salts such as $[I(C_6F_5)_2]OSO_2CF_3$ decompose above 250 °C [4]. Compounds containing the $[Te(C_6F_5)_3]^+$ cation have also been prepared and are part of our present investigations.

In the same manner as the thermal stabilities of all derivatives mentioned above increase, their reactivities also decrease.

Substituent effects at the phenyl groups, as observed especially for the derivatives $[XeAr]^+[BF_4]^-$ ($Ar = 2,6\text{-}F_2C_6H_3$, $2,4,6\text{-}F_3C_6H_2$) are notable [5]. The decomposition points of these derivatives are ca. 110 °C higher than that of $[XeC_6F_5]^+[BF_4]^-$. This increased stability may be associated with a back-donation of the F-2,6 atoms to the positively charged xenon atom. This effect is also demonstrated by the results of the X-ray crystal structure analysis of $[Xe(2,6\text{-}F_2C_6H_3)][BF_4]$. The F−Xe distances in this molecule are ca. 70 pm shorter than the sum of the van der Waals radii.

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