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$F_xXe(OTeF_5)_{3-x}^+$, $O{=}XeF_x(OTeF_5)_{3-x}^+$ (*x* = 0–2), and $O_2XeOTeF_5^+$ Cations: Their Preparation and Characterization in Solution by ^{129}Xe and ^{19}F NMR Spectroscopy

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Solvolysis reactions of the parent compounds, $Xe(OTeF_5)_4$ and $O{=}Xe(OTeF_5)_4$, in the strong $F/OTeF_5$ acceptor solvent SbF_5, led to $OTeF_5/F$ ligand redistribution and formation of two series of novel mixed-xenon cations, $F_xXe(OTeF_5)_{3-x}^+$, $O{=}XeF_x(OTeF_5)_{3-x}^+$ ($x = 0$–2), and $O_2XeOTeF_5^+$. The previously known XeF_3^+, $XeOF_3^+$, and XeO_2F^+ cations were observed in addition to the mixed cations. Decomposition of $O{=}XeF_2OTeF_5^+$ and $O{=}XeF(OTeF_5)_2^+$ in SbF_5 solution led respectively to formation of the previously known XeO_2F^+ cation and its novel $OTeF_5$ analog $O_2XeOTeF_5^+$. The $O{=}Xe(OTeF_5)_3^+$ cation was not observed in the $O{=}Xe(OTeF_5)_4/SbF_5$ systems but was prepared by allowing $O{=}Xe(OTeF_5)_4$ and "$Sb(OTeF_5)_5$" to react in SO_2ClF. All three series of cations have been characterized in solution by ^{129}Xe and ^{19}F NMR spectroscopy.

Introduction

Cationic xenon species have been known for some time,[2] and with the exception of Xe(VIII), representative examples can be found for each of the positive oxidation states of xenon, e.g., XeF^+,[3] XeF_3^+,[4] XeF_5^+,[5] $O{=}XeF_3^+$,[6] and XeO_2F^+.[7] In addition to binary and ternary fluoride and oxofluoride cations, several examples are known where xenon(II) is bonded to an oxygen or nitrogen atom of a suitably electronegative ligand group, i.e., $XeOTeF_5^+$,[8,9] $XeOSO_2F^+$,[9] $XeOSeF_5^+$,[10] and $XeN(SO_2F_2)_2^+$.[11] The novel nitrogen-bonded nitrile cations $RC{\equiv}NXeF^+$ (R = H, CH_3, CH_2F, C_2H_5, CF_3, C_2F_5, *n*-C_3F_7, or C_6F_5),[12,13] the perfluoropyridine cations 4-$RC_5F_4NXeF^+$ (R = F or CF_3),[14] the *s*-trifluorotriazine cation *s*-$C_3F_3N_2NXeF^+$,[13] and the first example of a Xe—C-bonded species, the pentafluorophenyl xenon(II) cation, $C_6F_5Xe^+$, have recently been reported,[15,16] along with the crystal structure for $[C_6F_5XeNCCH_3]^+[BF_2(C_6F_5)_2]^-$.[17] The $OTeF_5$ ligand has previously been shown to possess an effective group electronegativity only slightly less than that of fluorine,[18] and as a result, this group is capable of stabilizing almost all the same oxidation states as fluorine, including those of Xe and Kr. Thus, the neutral compounds $Xe(OTeF_5)_2$,[19] $Kr(OTeF_5)_2$,[20] $Xe(OTeF_5)_4$,[21] $O{=}Xe(OTeF_5)_4$,[21] and $O_2Xe(OTeF_5)_2$[22] have been characterized previously, as well as the mixed $F/OTeF_5$ derivatives $FXeOTeF_5$,[23] $O_2XeF(OTeF_5)$,[22] $XeF_n(OTeF_5)_{4-n}$,[22] and $O{=}XeF_n(OTeF_5)_{4-n}$.[21,22] In addition, examples of $F/OTeF_5$ redistributions have been reported for compounds of other elements, resulting in the formation of the series of mixed species $UF_n(OTeF_5)_{6-n}$,[24] $WF_n(OTeF_5)_{6-n}$,[25] $O{=}MoF_n(OTeF_5)_{4-n}$,[26] $IF_n(OTeF_5)_{4-n}$,[27] $TeF_n(OTeF_5)_{4-n}$,[28,29] and $TeF_n(OTeF_5)_{3-n}^+$.[29]

Prior to the present work, no $OTeF_5$-substituted cations were known containing xenon in an oxidation state higher than +2. Owing to its high effective electronegativity, the $OTeF_5$ group seemed the most likely ligand to stabilize mixed $F/OTeF_5$ Xe(IV) and Xe(VI) cations. The only previously known example of a noble-gas cation containing the $OTeF_5$ group was the $XeOTeF_5^+$ cation.[8,9]

Results and Discussion

Formation of the $F_xXe(OTeF_5)_{3-x}^+$, $O{=}XeF_y(OTeF_5)_{3-y}^+$ (x = 0–2, y = 1–3), and $O_2XeF_z(OTeF_5)_{1-z}^+$ (z = 0, 1) Cations in SbF_5 Solution. Since SbF_5 can act as a fluorinating agent as well as a strong acceptor, a large number of mechanistic alternatives could account for the formation of the $F_xXe(OTeF_5)_{3-x}^+$ and $O{=}XeF_y(OTeF_5)_{3-y}^+$ (x = 0–2, y = 1–3) cations observed in the present study. Reaction sequences leading to the formation of the $F_xXe(OTeF_5)_{3-x}^+$ and $O{=}XeF_y(OTeF_5)_{3-y}^+$ cations most likely involve the initial formation of $Xe(OTeF_5)_3^+$ and $O{=}Xe(OTeF_5)_3^+$ by transfer of an $OTeF_5$ group to the powerful Lewis acid, SbF_5, which is followed by $F/OTeF_5$ ligand scrambling according to equilibrium 1, where x = 0–3, p = 0 or 1, m = 0–5, and n = 1, 2, 3, ...

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$$O_pXeF_x(OTeF_5)_{4-x} + n[SbF_{5-m}(OTeF_5)_m] \rightleftharpoons O_pXeF_x(OTeF_5)_{3-x}{}^+ + Sb_nF_{(5n+1)-m}(OTeF_5)_m{}^- \quad (1)$$

While solutions of $Xe(OTeF_5)_4$ and $O{=}Xe(OTeF_5)_4$ in SbF_5 at 5 °C were found to give rise to series of mixed $F/OTeF_5$ cations, these solutions also underwent slow decomposition. The observation of slow gas evolution in both systems at 5 °C, as well as the presence of TeF_6, XeF^+, $XeOTeF_5{}^+$, O_2XeF^+, and the novel $O_2XeOTeF_5{}^+$ cation (Table I) is consistent with the decomposition reactions represented by eqs 2 and 3. An analogous decomposition

$$O{=}XeF_2OTeF_5{}^+ \rightarrow O_2XeF^+ + TeF_6 \quad (2)$$

$$O{=}XeF(OTeF_5)_2{}^+ \rightarrow O_2XeOTeF_5{}^+ + TeF_6 \quad (3)$$

$$FI(OTeF_5)_4 \rightarrow O{=}I(OTeF_5)_3 + TeF_6 \quad (4)$$

involving oxygen transfer and fluorination of the $OTeF_5$ group has been reported previously for $FI(OTeF_5)_4$ (eq 4).[27] Since the O_2XeF^+ cation has previously been shown to undergo decomposition by oxidative elimination of O_2 with the formation of the XeF^+ cation according to eq 5,[7] it is reasonable to expect the new $O_2XeOTeF_5{}^+$ cation to decompose in a similar fashion according to eq 6.

$$O_2XeF^+ \rightarrow O_2 + XeF^+ \quad (5)$$

$$O_2XeOTeF_5{}^+ \rightarrow O_2 + XeOTeF_5{}^+ \quad (6)$$

Although the presence of XeF^+ was established by ^{19}F NMR spectroscopy, its ^{129}Xe resonance was presumably too broad to be observed. The $XeOTeF_5{}^+$ cation was, however, detected as a decomposition product by ^{129}Xe NMR spectroscopy (Table I). The $XeF_x(OTeF_5)_{3-x}{}^+$ cations undergo decomposition reactions (eqs 7–9) that are analogous to those of $O{=}XeF_x(OTeF_5)_{3-x}{}^+$ (cf. eqs 2, 3, and 10 and Table I).

$$\begin{tikzcd}
F_2XeOTeF_5{}^+ \arrow[r] & {[OXeF^+] + TeF_6} \arrow[d] & (7) \\
 & \tfrac{1}{2}O_2 + XeF^+ &
\end{tikzcd}$$

$$\begin{tikzcd}
FXe(OTeF_5)_2{}^+ \arrow[r] & {[OXeOTeF_5{}^+] + TeF_6} \arrow[d] & (8) \\
 & \tfrac{1}{2}O_2 + XeOTeF_5{}^+ &
\end{tikzcd}$$

$$\begin{tikzcd}
Xe(OTeF_5)_3{}^+ \arrow[r] & {[OXeOTeF_5{}^+] + F_5TeOTeF_5} \arrow[d] & (9) \\
 & \tfrac{1}{2}O_2 + XeOTeF_5{}^+ &
\end{tikzcd}$$

However, unlike the Xe(VI) dioxo cations formed in reactions 2 and 3, the Xe(IV) cations $O{=}XeF^+$ and $O{=}XeOTeF_5{}^+$ are expected to be very unstable[30] and presumably undergo rapid decomposition according to eqs 7–9 also with the formation of O_2, TeF_6, $F_5TeOTeF_5$, XeF^+, and $XeOTeF_5{}^+$ (Table I). Although the ^{19}F NMR spectra are complicated by overlapping AB_4 multiplets, the intense AB_4 pattern attributable to $F_5TeOTeF_5$ and the intense singlet of TeF_6 with its characteristic ^{125}Te satellites were readily assigned by comparison with the literature values.[9,20] The AB_4 spectrum of $F_5TeOTeF_5$ is closely overlapped by weaker AB_4 pattens which are believed to arise from $TeF_n(OTeF_5)_{6-n}$ (where $n < 5$).[20]

Attempted Isolation of the $O{=}Xe(OTeF_5)_3{}^+$ and $Xe(OTeF_5)_3{}^+$ Cations. The isoelectronic iodine(V) analogs of $O{=}Xe(OTeF_5)_3{}^+$ and $Xe(OTeF_5)_3{}^+$, namely, $O{=}I(OTeF_5)_3$ and $I(OTeF_5)_3$, have been reported previously as stable species.[27,31] While $Xe(OTeF_5)_3{}^+$ is relatively stable in SbF_5 at 5 °C, the $O{=}Xe(OTeF_5)_3{}^+$ cation has not been observed for solutions of $O{=}Xe(OTeF_5)_4$ in SbF_5. The latter cation appears to be unstable under these conditions, decomposing according to eq 10 by the elimination of the oxo compound, $F_5TeOTeF_5$.

$$O{=}Xe(OTeF_5)_3{}^+ \rightarrow O_2XeOTeF_5{}^+ + F_5TeOTeF_5 \quad (10)$$

Although the ^{19}F NMR spectra are complicated by overlapping AB_4 multiplets, intense resonances attributable to the A and B_4 parts of the $F_5TeOTeF_5$ spectrum were found to be present along with weaker overlapping AB_4 spectra corresponding to other members of the series $TeF_n(OTeF_5)_{6-n}$.[20] The $O_2XeOTeF_5{}^+$ cation was observed as the dominant cation in the ^{19}F and ^{129}Xe NMR spectra (Table I). The problems associated with the thermal instability of $O{=}Xe(OTeF_5)_3{}^+$ were overcome by preparing the cation at lower temperatures (−80 and −60 °C) in SO_2ClF solvent according to eq 11 and equilibrium 12. The ^{129}Xe NMR spectrum consisted of two resonances corresponding to free $O{=}Xe(OTeF_5)_4$ in equilibrium with $O{=}Xe(OTeF_5)_3{}^+$ (vide infra).

$$Xe(OTeF_5)_2 + Sb(OTeF_5)_3 \rightarrow \text{“}Sb(OTeF_5)_5\text{”} + Xe \quad (11)$$

$$\text{“}Sb(OTeF_5)_5\text{”} + O{=}Xe(OTeF_5)_4 \rightleftharpoons O{=}Xe(OTeF_5)_3{}^+Sb(OTeF_5)_6{}^- \quad (12)$$

The thermal instability of the $O{=}Xe(OTeF_5)_3{}^+$ cation, which was indicated by the complexity of the ^{19}F NMR spectrum in the F-on-Te(VI) region of the spectrum, precluded isolation of the salt $O{=}Xe(OTeF_5)_3{}^+Sb(OTeF_5)_6{}^-$.

An analogous attempt to prepare $Xe(OTeF_5)_3{}^+Sb(OTeF_5)_6{}^-$ failed. The ^{129}Xe NMR spectrum of $Xe(OTeF_5)_4$ and “$Sb(OTeF_5)_5$” (see Experimental Section) in SO_2ClF at −25 °C consisted of only the $Xe(OTeF_5)_4$ spectrum [$\delta(^{129}Xe) = -601.3$ ppm, $^3J(^{129}Xe\text{–}F_e) = 58$ Hz, $^2J(^{129}Xe\text{–}^{125}Te) = 1000$ Hz). No $XeOTeF_5{}^+$ was observed in the ^{129}Xe spectrum indicating $Xe(OTeF_5)_3{}^+$ cannot have been formed (cf. eq 9). Like XeF_4, which forms stable $XeF_3{}^+$ salts with SbF_5 but not with the weaker fluoride ion acceptor AsF_5,[32] $Xe(OTeF_5)_4$ does not interact with the weaker $OTeF_5$ acceptor, “$Sb(OTeF_5)_5$”, to give the $Xe(OTeF_5)_3{}^+Sb(OTeF_5)_6{}^-$ salt but behaves as an $OTeF_5$ donor toward the stronger acceptor, SbF_5, to give a mixed $F/OTeF_5$ polyanion salt of $Xe(OTeF_5)_3{}^+$ in SbF_5 solution (vide infra).

NMR Spectroscopy. The characterization of the species in the series $F_xXe(OTeF_5)_{3-x}{}^+$ and $O{=}XeF_y(OTeF_5)_{3-y}{}^+$ ($x = 0$–2, $y = 1$–3), generated in situ, in neat SbF_5 was achieved by ^{129}Xe and ^{19}F NMR spectroscopy. The $O_2XeF_z(OTeF_5)_{1-z}{}^+$ ($z = 0, 1$) cations result from the decomposition of $O{=}XeF_y(OTeF_5)_{3-y}{}^+$ ($y = 1, 2$) (eqs 2 and 3). A reaction temperature of 5 °C was found to provide the most desirable compromise between the reduced solubility of $Xe(OTeF_5)_4$ and $O{=}Xe(OTeF_5)_4$ in SbF_5 at lower temperatures and slow decomposition rates of the cations at higher temperatures.

$O{=}XeF_y(OTeF_5)_{3-y}{}^+$ ($y = 1$–3) and $O_2XeF_z(OTeF_5)_{1-z}$ ($z = 0, 1$) Cations Generated in SbF_5 Solvent. The individual cations of the $O{=}XeF_y(OTeF_5)_{3-y}{}^+$ series were identified in the ^{129}Xe and ^{19}F NMR spectra of $O{=}Xe(OTeF_5)_4$ dissolved in neat SbF_5 at 5 °C. The ^{129}Xe NMR spectra of the title species are depicted in Figure 1a,b, respectively, and their chemical shifts and coupling constants are summarized in Table I. In Figure 1a, two major components and one minor component can be identified. At highest frequency, a doublet of triplets [$\delta(^{129}Xe) = 242.8$ ppm,

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(30) Attempts to prepare $O{=}XeF^+AsF_6{}^-$ by direct combination of $XeOF_2$ with AsF_5 at −78 °C resulted in explosions. Gillespie, R. J.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1977**, 595.

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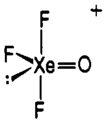
Table I. ^{129}Xe and ^{19}F NMR Parameters for Xenon Cations Observed for $Xe(OTeF_5)_4$ and $O{=}Xe(OTeF_5)_4$ Solutions in SbF_5 Solvent[a]

solute	species	chemical shift[b] (ppm)		coupling constant (Hz)
		$\delta(^{129}Xe)$	$\delta(^{19}F)$[c]	$^1J(^{129}Xe–^{19}F)$
$Xe(OTeF_5)_4$[d]	$Xe(OTeF_5)_3^+$	–341.9		
	$FXe(OTeF_5)_2^+$	–178.4	49.3	2900
	$F_2XeOTeF_5^+$	22.4	26.8	2893
	$F_5TeOTeF_5$[e]	–51.5 (A) –42.5 (B_4)		
	TeF_6[f]		–56.4	
$O{=}Xe(OTeF_5)_4$	$O{=}XeF(OTeF_5)_2^+$	60.6	129.2	1089
	$O{=}XeF_2OTeF_5^+$[g]	121.3	136.9 (F on Xe) –60.5 (A) –21.2 (X_4)	796
	$O{=}XeF'F_2^+$[h]	242.8	189.6 (F′) 143.9 (F)	1021 496
	$O_2XeOTeF_5^+$	543.0		
	O_2XeF^+	704.3	195.7	95
	$XeOTeF_5^+$	–1481.9		
	XeF^+[i]		–259	
	$F_5TeOTeF_5$		–51.9 (A) –42.6 (B_4)	
	TeF_6[f]		–56.5	

[a] SbF_5 solvent lines were broad and occurred at –86.0, –94.6, –104.7, and –131.8 ppm in the ^{19}F NMR spectra. [b] Spectra were recorded in SbF_5 solvent at 5 °C and referenced externally with respect to neat liquid $XeOF_4$ (^{129}Xe) and $CFCl_3$ (^{19}F) at 24 °C; a positive (negative) chemical shift denotes a resonance to high (low) frequency of the reference substance. [c] In the majority of cases, owing to the complexity of the overlapping AB_4 spectra in the F-on-Te(VI) region of the ^{19}F NMR spectrum, only F-on-Xe resonances are reported. [d] The ^{129}Xe and ^{19}F resonances arising from XeF^+ are presumed to have been too broad to be observed in this system. [e] $^2J(^{19}F_A–^{19}F_B)$ = 180 Hz. [f] $^1J(^{125}Te–^{19}F)$ = 3722 Hz. [g] $^2J(^{19}F_A–^{19}F_X)$ = 165 Hz. [h] $^2J(^{19}F–^{19}F')$ = 88 Hz. [i] The ^{19}F resonance arising from XeF^+ was broad ($\nu_{1/2}$ = 550 Hz) and was presumably too broad to be observed in the ^{129}Xe NMR spectrum.

$^1J(^{129}Xe–^{19}F')$ = 1021 Hz, $^1J(^{129}Xe–^{19}F)$ = 496 Hz) is assigned to $O{=}XeF_3^+$ (structure I) by comparison with the literature NMR parameters for this species.[33,34] The major component in the ^{129}Xe NMR spectrum is a triplet [$\delta(^{129}Xe)$ = 121.3 ppm, $^1J(^{129}Xe–^{19}F)$ = 796 Hz], which is assigned to the difluoro species, $O{=}XeF_2OTeF_5^+$ and is consistent with a trigonal-bipyramidal arrangement of four ligands and a lone pair of electrons around xenon, with the two fluorine atoms occupying the axial positions (structure II), in accord with the predictions of the valence shell electron pair repulsion rules.[35] The minor component in the spectrum is a doublet [$\delta(^{129}Xe)$ = 60.6 ppm, $^1J(^{129}Xe–^{19}F)$ = 1089 Hz] and is assigned to the monofluoro species, $O{=}XeF(OTeF_5)_2^+$ (structure III).



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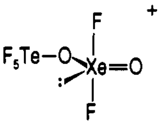

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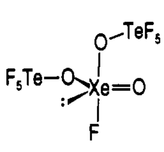

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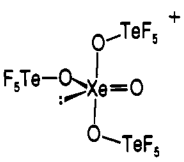

IV

In Figure 1b, the doublet is attributed to O_2XeF^+ [$\delta(^{129}Xe)$ = 704.3 ppm, $^1J(^{129}Xe–^{19}F)$ = 95 Hz] (structure V) and the singlet is ascribed to $O_2XeOTeF_5^+$ [$\delta(^{129}Xe)$ = 543.0 ppm] (structure VI). A singlet was also observed in the Xe(II) region of the spectrum and is assigned to $XeOTeF_5^+$ [$\delta(^{129}Xe)$ = –1481.9 ppm]. Comparisons between these NMR parameters and those reported previously confirm the assignments for O_2XeF^+ [8] and $XeOTeF_5^+$.[10] The assignment of $O_2XeOTeF_5^+$ is made

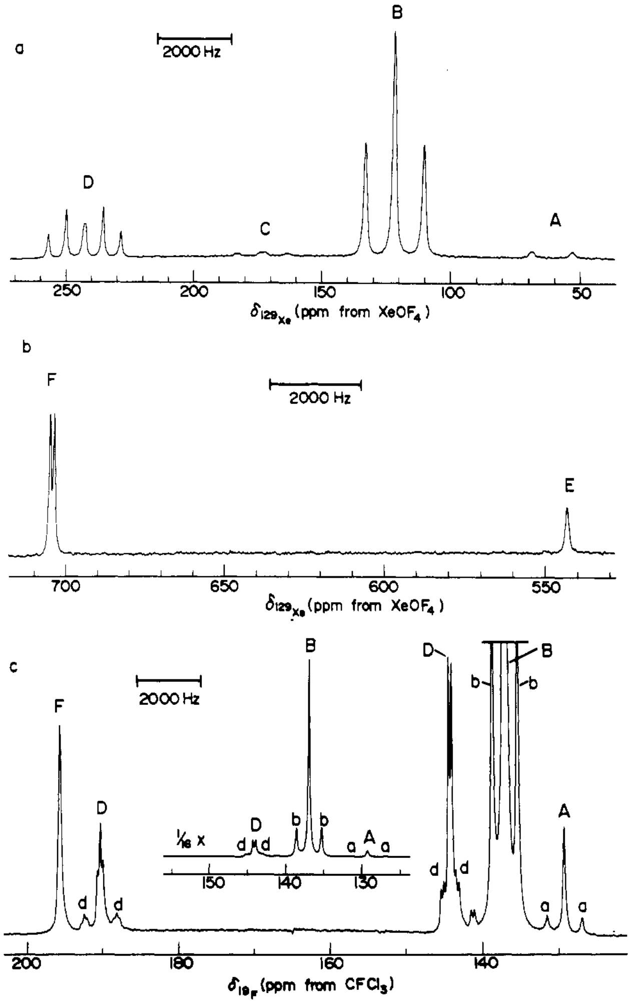

Figure 1. NMR spectra of $O{=}Xe(OTeF_5)_4$ in SbF_5 obtained at 5 °C. (a, b) ^{129}Xe spectra, 69.56 MHz: (A) $O{=}XeF(OTeF_5)_2^+$; (B) $O{=}XeF_2OTeF_5^+$; (C) unknown; (D) $O{=}XeF_3^+$; (E) $O_2XeOTeF_5^+$; (F) O_2XeF^+. (c) ^{19}F spectrum, 235.36 MHz (lowercase letters denote ^{129}Xe satellites): (A) $O{=}XeF(OTeF_5)_2^+$; (B) $O{=}XeF_2OTeF_5^+$; (D (d,d)) $O{=}XeF_3^+$; (F) O_2XeF^+.

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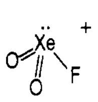

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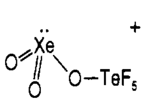


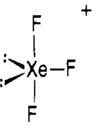
VI

without the benefit of previously reported spectra; however, a singlet in the ^{129}Xe NMR spectrum to low frequency of the O_2XeF^+ resonance is consistent with this species and with well-established chemical shift trends.[22,36]

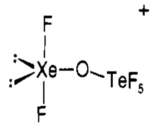
The ^{19}F NMR spectrum for the F-on-Xe region is depicted in Figure 1c and corroborates the assignments made in the ^{129}Xe NMR spectrum. The ^{19}F NMR parameters for known species, O_2XeF^+ [$\delta(^{19}F) = 195.7$ ppm] and $O{=}XeF'F_2^+$ [$\delta(^{19}F') = 189.6$ ppm, $\delta(^{19}F) = 143.9$ ppm], are in agreement with literature values.[7] The assignments of resonances attributed to the new cations, $O{=}XeF_2OTeF_5^+$ and $O{=}XeF(OTeF_5)_2^+$, were confirmed by comparison of their relative intensities and ^{129}Xe satellite spacings with those observed in the ^{129}Xe NMR spectra.

Identification of the $O{=}Xe(OTeF_5)_3^+$ Cation in SO_2ClF Solution. The ^{129}Xe NMR spectrum of a mixture of $O{=}Xe(OTeF_5)_4$ and "$Sb(OTeF_5)_5$" in SO_2ClF at −78 °C shows an intense multiplet [$^3J(^{129}Xe-^{19}F) = 41$ Hz] with accompanying ^{125}Te satellites [$^2J(^{129}Xe-^{125}Te) = 1618$ Hz] at $\delta = -170.3$ ppm, which is attributable to $O{=}Xe(OTeF_5)_4$. In addition, a new, very weak resonance was observed at higher frequency ($\delta = -1.9$ ppm). On warming of the sample to −50 °C and then to −30 °C, a clear pale yellow solution resulted. The ^{129}Xe NMR spectrum revealed that the new resonance had increased in intensity, and ^{125}Te satellites [$^2J(^{129}Xe-^{125}Te) = 1245$ Hz] flanking the central resonance could now be observed (Figure 2). The new peak is assigned to the $O{=}Xe(OTeF_5)_3^+$ cation (structure IV) on the basis of its high-frequency chemical shift which fits in well with the ^{129}Xe chemical shifts observed for the other cations in the $O{=}XeF_n(OTeF_5)_{4-n}$ series (see below). Finally, the sample was warmed to −10 °C for 20 min and the spectrum recorded at −60 °C. Again the resonance due to the $O{=}Xe(OTeF_5)_3^+$ cation had grown and now had an intensity one-third that of the $O{=}Xe(OTeF_5)_4$.

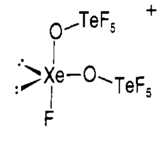
$F_xXe(OTeF_5)_{3-x}^+$ Cations ($x = 0$–2) Generated in SbF_5 Solvent. Figure 3 depicts the Xe(IV) region of the ^{129}Xe NMR spectrum resulting from the reaction of $Xe(OTeF_5)_4$ with SbF_5. The ^{129}Xe and ^{19}F NMR parameters for this system, recorded at 5 °C, are summarized in Table I. Three species are observed in the ^{129}Xe NMR spectrum; no detectable amount of the XeF_3^+ cation (structure VII) was observed. At highest frequency, the intense triplet [$\delta(^{129}Xe) = 22.4$ ppm, $^1J(^{129}Xe-^{19}F) = 2893$ Hz] is assigned to the difluoro species, $F_2XeOTeF_5^+$ (structure VIII). Arguments similar to those used to assign $O{=}XeF_2OTeF_5^+$ in Figure 1a can also be employed in the assignment of $F_2XeOTeF_5^+$. Furthermore, a singlet resonance in the ^{19}F NMR spectrum [$\delta(^{19}F) = 26.8$ ppm], with accompanying ^{129}Xe satellites of the same magnitude as the ^{129}Xe triplet coupling, serve to confirm this assignment. A doublet resonance [$\delta(^{129}Xe) = -178.4$ ppm, $^1J(^{129}Xe-^{19}F) = 2900$ Hz] at midrange in the Xe(IV) region of the spectrum is assigned to $FXe(OTeF_5)_2^+$ (structure IX). Again, the ^{19}F NMR results (Table I) are consistent with the assignment to $FXe(OTeF_5)_2^+$. In Figure 2, the singlet ^{129}Xe resonance [$\delta(^{129}Xe) = -341.9$ ppm] is assigned to $Xe(OTeF_5)_3^+$ (structure X), which has a ^{129}Xe NMR resonance to lower frequency than the resonances of either $F_2XeOTeF_5^+$ or $FXe(OTeF_5)_2^+$, as is expected in view of the previously established additivity trends observed upon substitution of $OTeF_5$ for F in XeF_4, $O{=}XeF_4$, and O_2XeF_2.[22,35]



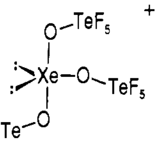
VII



VIII



IX



X

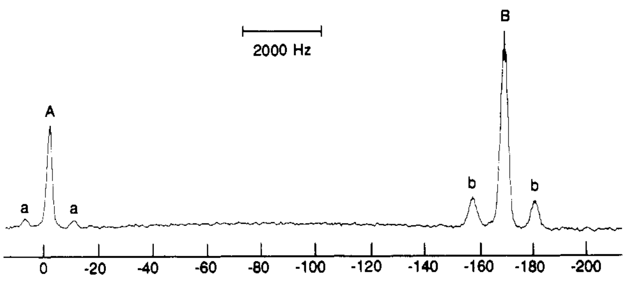


Figure 2. ^{129}Xe NMR spectrum obtained at 69.56 MHz and −78 °C of $O{=}Xe(OTeF_5)_4$ and "$Sb(OTeF_5)_5$" in SO_2ClF solvent (lowercase letters denote ^{125}Te satellites): (A) $O{=}Xe(OTeF_5)_3^+$; (B) $O{=}Xe(OTeF_5)_4$.

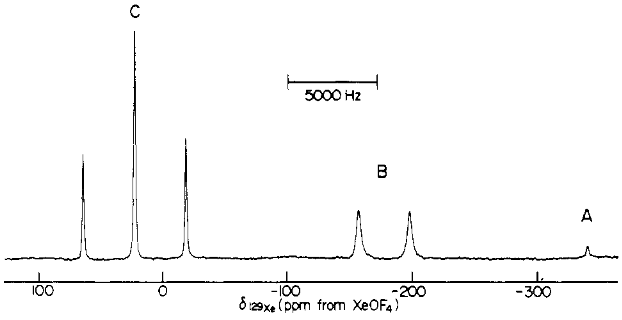


Figure 3. ^{129}Xe NMR spectrum obtained at 69.56 MHz and −5 °C of $Xe(OTeF_5)_4$ in SbF_5: (A) $Xe(OTeF_5)_3^+$; (B) $FXe(OTeF_5)_2^+$; (C) $F_2XeOTeF_5^+$.

Additivity among ^{129}Xe NMR Chemical Shifts. In order to complete and compare the trends among ^{129}Xe chemical shift data for both series of mixed cations, the ^{129}Xe chemical shifts of members of the series not present in the solutions resulting from the SbF_5 solvolysis reactions have been incorporated from other studies, i.e., XeF_3^+ in SbF_5 solvent from a previous study and $O{=}Xe(OTeF_5)_3^+$ recorded in SO_2ClF solvent in the course of the present work. Consequently, the chemical shift values may be expected to vary slightly from those that would be obtained from measurements in the same solution and in the same solvent medium.

In both series, $F_nXe(OTeF_5)_{3-n}^+$ and $O{=}XeF_n(OTeF_5)_{3-n}^+$, the ^{129}Xe NMR chemical shift becomes more positive as n increases. These trends are not unexpected, since, in all known examples, replacement of an $OTeF_5$ group by the more electronegative F atom results in deshielding of the xenon atom and an increase in the ^{129}Xe chemical shift. Schumacher and Schrobilgen[22] have shown in their study of the neutral series $F_nXe(OTeF_5)_{4-n}$, $O{=}XeF_n(OTeF_5)_{4-n}$, and $O_2XeF_n(OTeF_5)_{2-n}$, that the ^{129}Xe NMR chemical shifts are additive, becoming more positive as n increases, leading to average chemical shift changes of 211 for $XeF_{4-n}(OTeF_5)_n$, 44 for $O{=}XeF_{4-n}(OTeF_5)_n$, and 20 ppm/$OTeF_5$ group for $O_2XeF_{2-n}(OTeF_5)_n$.

In both series of cations, the ^{129}Xe NMR chemical shifts were also found to be additive (eqs 13 and 14), yielding average chemical shift changes of 182 ppm/$OTeF_5$ group for $XeF_{3-n}(OTeF_5)_n^+$ and 91 ppm/$OTeF_5$ group for $O{=}XeF_{3-n}(OTeF_5)_n^+$. The

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$$\delta(^{129}\mathrm{Xe})[\mathrm{XeF}_{3-n}(\mathrm{OTeF}_5)_n{}^+] = -182.2n + 198.3 \qquad R^2 = 0.998 \quad (13)$$

$$\delta(^{129}\mathrm{Xe})[\mathrm{O{=}XeF}_{3-n}(\mathrm{OTeF}_5)_n{}^+] = -91.1n + 232.7 \qquad R^2 = 0.982 \quad (14)$$

difference in average chemical shift change per $OTeF_5$ group between $XeF_{3-n}(OTeF_5)_n^+$ and $O{=}XeF_{3-n}(OTeF_5)_n^+$ is 91 ppm, whereas between the neutral analogs, $XeF_{4-n}(OTeF_5)_n$ and $O{=}XeF_{4-n}(OTeF_5)_n$, this difference was found to be 167 ppm.[22]

Experimental Section

Apparatus and Materials. All manipulations were carried out under anhydrous conditions on a vacuum line or in a nitrogen-filled drybox (Vacuum Atmospheres Model DLX).

Antimony pentafluoride (Ozark-Mahoning Co.) was purified by vacuum distillation prior to its use. Subsequent transfers to SbF_5 were performed with a glass-barrel syringe in the inert atmosphere of a drybox. The preparations of $Xe(OTeF_5)_2$,[37] $Xe(OTeF_5)_4$,[21,22] $O{=}Xe(OTeF_5)_4$,[21,22] and $Sb(OTeF_5)_3$[38] have been described previously.

NMR Sample Preparation. Solids were weighed and transferred into 9-mm-o.d. FEP NMR tubes, which were heat-sealed at one end and connected through 45° SAE flares to Kel-F valves. Antimony pentafluoride was syringed into the NMR tubes containing the solute cooled to −196 °C. Finally, the tubes were removed from the drybox while being cold- and heat-sealed under dynamic vacuum at −196 °C. Samples for the characterization of the $O{=}Xe(OTeF_5)_3^+$ cation were prepared in two stages. First, a solution of "$Sb(OTeF_5)_5$" in SO_2ClF was prepared by adding $Xe(OTeF_5)_2$ (0.14786 g, 0.2430 mmol) to $Sb(OTeF_5)_3$ (0.19024 g, 0.2271 mmol) contained in a 9-mm-o.d. FEP NMR tube held at −196 °C. The tube was fitted with a Kel-F valve, removed from the cold well of the drybox, and attached to a glass vacuum line and SO_2ClF (ca. 1.5 mL) distilled onto the solids at −196 °C. The mixture was warmed to 0 °C for between 3 and 8 min, during which time Xe gas evolution was observed and the solution took on a yellow coloration. This solution has been shown to contain an equimolar mixture of $XeOTeF_5^+Sb(OTeF_5)_6^-$ and $Sb(OTeF_5)_3$ which behaves as though it were $Sb(OTeF_5)_5$.[39] The solution was frozen to −196 °C in the drybox and $O{=}Xe(OTeF_5)_4$ (0.250 74 g, 0.2276 mmol) added to the mixture. The tube was evacuated, heat-sealed, and stored at −196 °C until the spectra could be run. The analogous reaction was attempted using $Xe(OTeF_5)_4$ in a effort to form the $Xe(OTeF_5)^+$ cation in SO_2ClF at low temperature. Stoichiometric amounts of reactants were used with molar quantities similar to those specified for the $O{=}Xe(OTeF_5)_4$/"$Sb(OTeF_5)_5$" system.

Nuclear Magnetic Resonance Spectroscopy. All NMR spectra were recorded unlocked (field drift < 0.1 Hz h^{-1}) on a Bruker WM-250 spectrometer equipped with a 5.8719-T cryomagnet and an Aspect 2000 computer. For variable-temperature measurements, samples were kept cold (−196 or −78 °C) until immediately prior to their placement in the precooled NMR probe. Prior to data accumulation, the tubes were allowed to equilibrate in the probe for several minutes while spinning. Temperatures were periodically checked by placing a copper–constantan thermocouple into the sampling region of the probe and were considered to be accurate to within ±1 °C.

The ^{129}Xe NMR spectra were obtained using a 10-mm probe (broadbanded over the frequency range 23–103 MHz) and tuned to 69.561 MHz. The ^{19}F NMR spectra were obtained on the same probe using the ^1H decoupler coils retuned to 235.361 MHz as the observe coils. Xenon-129 spectra were acquired in 400–10 000 transients at a spectral width of 100 kHz (32K memory, 6.1 Hz/data point, 0.164-s acquisition time). Fluorine-19 spectra were acquired in 64–1600 transients at a spectral width of 100 kHz (32K memory, 6.1 Hz/data point, 0.164-s acquisition time). Pulse widths corresponding to bulk magnetization tip angles, $\theta = 90°$, were 2 (^{19}F) and 22 μs (^{129}Xe).

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