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ON THE EXISTENCE OF THE TRIFLUOROXENATE (II) ION, XeF_3^- : COMMENTS ON
"THE 'BASE CATALYZED' FLUORINATION OF SO_2 BY XeF_2 " *

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SUMMARY

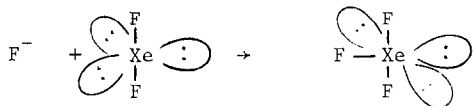
Conflicting data on the existence of the trifluoroxenate (II) ion, XeF_3^- , is analyzed. In particular, lack of isotope exchange and new spectroscopic lines in $\text{XeF}_2 + \text{F}^-$ reactions, negative ion mass spectra of xenon fluorides and the " 'Base Catalyzed' Fluorination of SO_2 by XeF_2 " are discussed.

RESULTS AND DISCUSSION

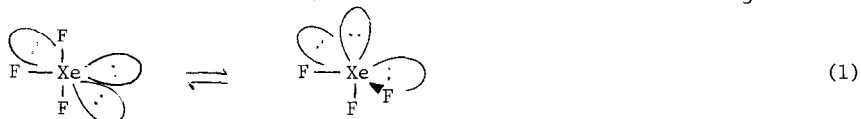
In this paper we wish to discuss the existence of the trifluoroxenate (II) ion, XeF_3^- . In 1963 it was suggested [1] as a plausible species by consideration of the diagonal rule and isoelectronic comparisons. Yet no salts of this ion have so far been isolated, in contrast to the octafluoroxenate (VI) ion, $\text{XeF}_8^{=}$ [2,3]. Furthermore, neither $^{18}\text{F} - ^{19}\text{F}$ exchange [4] nor new spectroscopic lines [5] has been observed in aqueous solutions of XeF_2 and F^- . However, Wilson [6] recently suggested XeF_3^- is an intermediate in the " 'base catalyzed' fluorination of SO_2 by XeF_2 ". It seems desirable to reconcile Wilson's mechanistic conclusions with the above seeming nonexistence of the anion of interest.

* The current paper may be considered as belonging to two series: Nucleophilic Displacement on Fluorine III [paper II: J. F. Liebman, J. Fluor. Chem., 5, 55 (1975)] and Conceptual Problems in Noble Gas and Fluorine Chemistry IV [paper III: Inorg. Nucl. Chem. Lett., 11, 687 (1975)].

What is presumably meant by XeF_3^- is an anion with three well-defined xenon-fluorine bonds. By Nyholm-Gillespie theory [7], such an anion would be expected to be T-shaped, i.e. pseudoöctahedral, with three lone pairs:



It is well established that octahedral and pseudoöctahedral species rarely pseudorotate [8]. Indeed, such pseudorotation would be a highly energetic process (1) as it would convert the above T to a pyramidal XeF_3^- with accompanying lone pair - lone pair repulsion. Should T shaped XeF_3^- be



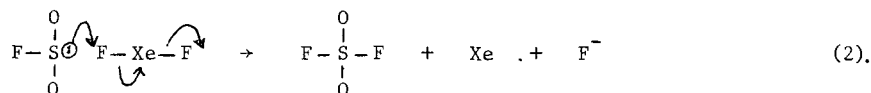
formed from reaction of XeF_2 and F^- , we thus anticipate it would decompose by loss of the equatorial fluorine. Loss of an axial fluorine would either yield a V shaped XeF_2^* of high energy, or produce the customary linear XeF_2 by a relatively undesirable non-least-motion process [9]. As such, we are led to assume that the fluorine lost from XeF_2 in reforming XeF_2 is the same fluorine originally added. It thus follows that lack of isotope exchange tells little about the existence of XeF_3^- . More precisely, we may preclude only the existence of a symmetric ion as earlier noted by Appelman [4].

We note at this time that XeF_3^- has been experimentally observed in the negative ion mass spectra of various xenon fluorides [10]. In these spectra, XeF^- has also been detected. XeF^- is isoelectronic with the essentially unbound Xe_2 and so is presumably bound by ion-induced dipole forces. This suggests that gas phase XeF_2 and F^- may well be bound only by analogous weak forces, say ion-quadrupole. This is in distinction to the formation of a third Xe-F bond of comparable strength (ca. 30 kcal/mole) [11,12] and length (ca. 2 Å) to the isolated binary xenon fluorides, XeF_2 , XeF_4 and XeF_6 [3,12].

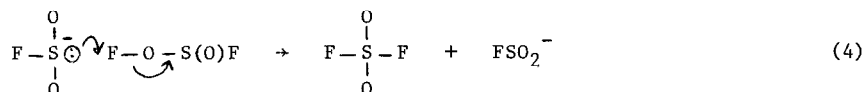
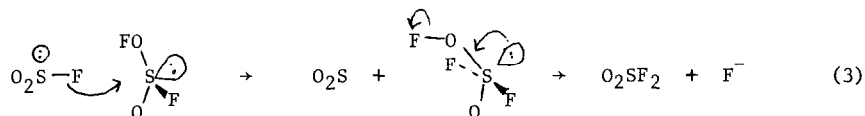
Let us now turn to Wilson's [6] mechanisms and suggest an alternative.

* While we have no data as to the difference in energy between the linear and V shaped XeF_2 , the difference in energy between the (ground state) V and linear conformation of ClF_2^+ has been indirectly determined to be ca. 50 kcal/mole (R. W. Shaw, Jr., T. X. Carroll and T. D. Thomas, J. Amer. Chem. Soc., 95, 5870 (1973)).

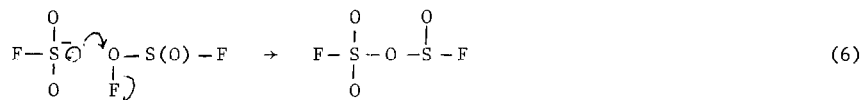
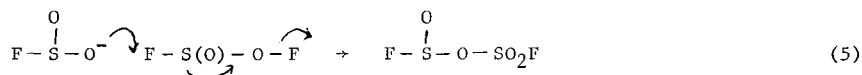
It appears somewhat surprising to invoke SO^{+2} , SO_2F^- and XeF_3^- in reasonable concentrations in the same solution -- SO^{+2} is the "acid" form of SO_2 , while SO_2F^- (and XeF_3^-) correspond to the "basic" form. This alone, of course, does not disqualify the mechanism or exclude the existence of XeF_3^- . However, it is instructive to consider alternate mechanisms which do not include XeF_3^- and which are somewhat more consistent with the known chemistry of the species of interest. We will naturally consider the SO_2F^- anion as being present as this arises from the solvation reaction of F^- in liquid SO_2 . We anticipate an $\text{S}_{\text{N}}2(\text{F})$ reaction [13] of SO_2F^- and XeF_2 will yield SO_2F_2 , Xe and F^- :



This is in opposition to forming an intermediate fluorosulfinate, $\text{FS}(\text{O})\text{XeF}$. (The related fluorosulfonate is well established [14].) This reaction is suggested by the fluorination of ClO_3^- , isoelectronic with SO_2F^- , with F_2 to form ClO_3F [15]. We note the corresponding reaction of BrO_3^- does not form BrO_3F [16] despite its inherent stability [17]. This is explicable in terms of the intermediacy of the hypofluorite, BrO_2OF [13]. This suggests that both isomers, SO_2F_2 or sulfonyl fluoride, and $\text{FS}(\text{O})\text{OF}$ or fluorosulfinyl hypofluorite may well be formed by oxidative fluorination of SO_2F^- . While there is controversy about a related pair of isomers, NO_2F and ONOF [18,19, 20], it is to be noted that the fluorosulfonyl hypofluorite, FSO_2OF , is well known [21]. We anticipate most of the $\text{FS}(\text{O})\text{OF}$ will isomerize to the indubitably more stable SO_2F_2 via formal "F⁻" or "F⁺" transfer (i.e. $\text{S}_{\text{E}}2(\text{F})$ or $\text{S}_{\text{N}}2(\text{F})$, reactions (3) and (4) respectively).



(A reaction analogous to (3) can occur with unsolvated F^- , as on the surface of solid CsF or other ionic fluorides.) However, alternative to both reactions is attack of the oxygen (or sulfur) in FSO_2^- on the sulfur (or oxygen) of $\text{FS}(\text{O})\text{OF}$ to form the mixed sulfinic-sulfonic anhydride (reactions 5 and 6).



The above anhydride might be expected to cleave under "basic" conditions to yield either SO_2F_2 and FSO_2^- or SOF_2 and FSO_3^- . Indeed, all four of these sulfur-oxygen-fluorine species were observed by Wilson [6]. A reaction corresponding to (5) but with FSO_3^- would yield $(\text{FSO}_2)_2\text{O}$, an observed product. However, as noted by Wilson, subsequent reactions of this anhydride would decrease its yield.

We now turn briefly to the reactions run in the presence of chloride ion. A reaction corresponding to (2) involving solvated chloride ion, i.e. ClSO_2^- , would yield SO_2ClF , an observed product. We note that organic compounds containing the ClSO_2 group, i.e. alkane or arenesulfonyl chlorides are known to yield the corresponding sulfonyl fluoride on reaction with XeF_2 [22]. Such a reaction of ClSO_2^- would yield FSO_2^- and so the above described reactions (2 - 6) would proceed. Indeed, the reaction of ClSO_2^- (or FSO_2^-) with XeF_2 to form SO_2ClF (or SO_2F_2) regenerates an equivalent amount of F^- . Since F^- is most probably solvated better than Cl^- (i.e. the concentration of FSO_2^- is higher than ClSO_2^-), it is not surprising that most of the observed products of the reaction of CsCl or $(\text{CH}_3)_4\text{NCl}$ mimic those of the corresponding fluoride.

In conclusion, it would appear that XeF_3^- is not a necessary intermediate in Wilson's reactions. While we hesitate to say this T shaped anion is nonexistent, we are doubtful it is of mechanistic consequence in noble gas chemistry to date.

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