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POSITIVE FLUORINE - REALITY OR MISCONCEPTION?

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SUMMARY

Polar covalence theory arguments are presented against the existence of a permanent positive polarization of fluorine in heteronuclear X-F molecules and against the existence of X groups having a higher electronegativity than fluorine itself. The heterolytic fission of fluorine and the possibility of inducing a positive fluorine dipole in X-F molecules with highly electro-negative X groups are briefly discussed.

INTRODUCTION

Fluorination reactions with highly electronegative compounds are frequently explained by invoking a positive fluorine. In a recent note [1], this author took exception to the postulate of positive fluorine by criticizing a recent paper of Cartwright and Woolf on this subject [2]. In the preceding paper [3], the same authors (C+W) summarized some arguments in favor of positive fluorine. Since the issue of a positive fluorine is largely a conceptual problem and is not readily accessible to direct experimental measurements, a speculative interpretation of the mechanism of poorly studied complex organic reactions has little merit. A systematic analysis of this problem therefore appeared more rewarding and is given below.

DISCUSSION

Definition of a Positive Fluorine

A positive fluorine is the direct result of a transfer of electron density in a covalent X-F bond from F to X resulting in the following polar covalence $\overset{\delta-}{X}-\overset{\delta+}{F}$, where XF can be either heteronuclear (X is different from F) or homonuclear (X equals F). If XF is homonuclear, i.e. F₂, one cannot have a permanent but only an induced dipole. If XF is heteronuclear, one can have both a permanent and an induced dipole. It should be noted that this dipole is not identical with the experimentally measurable overall dipole moment of the XF molecule due to other factors such as lone valence electron pair effects.

Definition of the Problem

The issue raised by us in our previous critique [1] was that there is no experimental and theoretical justification for the assumption of a permanent $\overset{\delta-}{X}-\overset{\delta+}{F}$ polarity in a heteronuclear XF molecule. Therefore, unless stated otherwise, the following arguments will be referring to this issue.

Theoretical Arguments

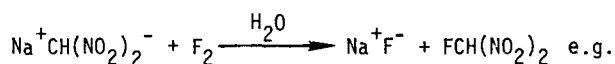
The assumption of a permanent positive fluorine dipole in a heteronuclear XF atom violates the principle of electronegativity equalization which was first published in 1951 by Sanderson [4] and proven correct by quantum mechanics in 1978 by Parr and coworkers [5] and in 1979 by Politzer and Weinstein [6]. This principle states that when two or more atoms unite to form a compound, their electronegativities become adjusted to the same intermediate value within the compound. In other words, the different kinds of atoms become equal in electronegativity by unequal sharing of the bonding electrons. This means that the more electronegative atom must acquire a negative charge and the less electronegative atom a positive charge. Since fluorine is without doubt the most electronegative element, a heteroatomic X-F bond can be permanently polarized in only one direction, i.e. $\overset{\delta+}{X}-\overset{\delta-}{F}$. This principle also rules out the possibility that X groups, such as CF₃O⁻, SeF₅O⁻, or TeF₅O⁻, which consist of fluorine substituted heteroatoms of lower electronegativity can become more electronegative than fluorine itself [1,7-10].

Experimental Arguments

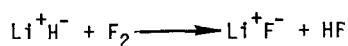
Electrophilic substitution reactions are not a convincing argument in favor of a positive fluorine. First of all, the mechanisms of most of these complex reactions have not been established. Secondly, in these reactions a strong electrophile attacks an electron rich center, and the polarity of the bonds within the electrophile is of lesser importance than other factors. In NF_4^+ , for example, the nitrogen atom is coordinatively saturated. Consequently, NF_4^+ can attack an electron rich center only through one of its fluorine ligands but not through its nitrogen atom. The fact that NF_4^+ can undergo electrophilic substitution reactions is therefore no indication for a positively polarized fluorine.

On the other hand, addition reactions in which a polar X-F molecule is added across a polar double bond, are capable of yielding information about the polarity of the X-F bond. Several such studies have recently been carried out using ClO_3OF [11], TeF_5OF , and CF_3OF [12] and did not provide any evidence for a positive fluorine in these hypofluorites.

One piece of experimental evidence for positive fluorine, cited by (C+W) is the selective substitution at acidic hydrogens,

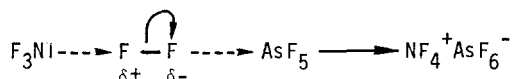


(C+W) concluded that, if half the fluorine becomes fluoride, by a simple charge-balance the other half must be positive fluorine. The shallowness of this conclusion can easily be demonstrated by the following analogous equation which would prove that the fluorine in HF must be positive.

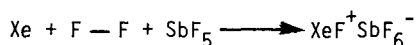


Induced Polarization and Heterolytic Fission of Fluorine

Although our original critique of the paper by (C+W) was only concerned with the permanent dipole of a heteronuclear XF molecule, the preceding paper [3] requires some comment on the heterolytic fission of fluorine. If in XF molecules X becomes more and more electronegative and eventually becomes F, the energy required to induce a dipole moment decreases and the possibility of forming an induced positive fluorine dipole increases. Although the formation of NF_4AsF_6 was originally postulated [13] to involve the heterolytic fission of F_2 ,



subsequent studies [14-16] have shown that the mechanism of this reaction is more complicated, requires predissociation of F_2 , and involves the formation of the NF_3^+ radical cation as an intermediate. However, if the hard Lewis base NF_3 is replaced by the soft base Xe, the following reaction proceeds spontaneously even in the dark [17].



It is likely that this reaction is a rare example of an actual heterolytic fission of fluorine and therefore involves a Lewis acid - Lewis base induced polarization of fluorine. However, the possible existence of such a reaction for homonuclear difluorine has no bearing on the formation of a permanent positive fluorine in the heteronuclear XF molecules discussed above.

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