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POSITIVE FLUORINE - MISCONCEPTION OR REALITY?

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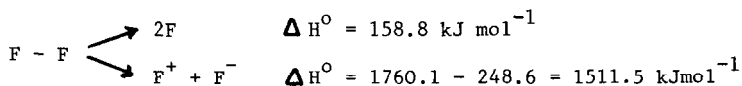
SUMMARY

Some of the evidence for positive fluorine is summarized. Evidence against positive fluorine based on the direction of addition to fluorolefins, and polarity as judged by electronegativity values, is queried.

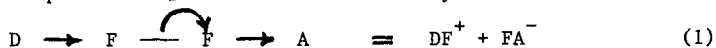
DISCUSSION

Christe's comments [1] on our paper [2] illustrates our point about the reluctance of many fluorine chemists to consider the possibility of positive fluorine even when presented with the type of evidence they would find acceptable for positive chlorine.

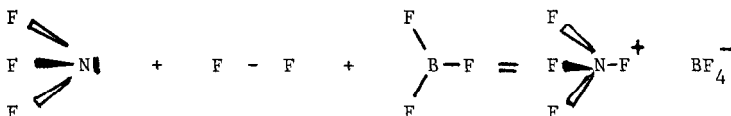
Before commenting on the results claimed to show the absence of positive fluorine, the experimental conditions required to encourage positive fluorine should be stated. The homolytic dissociation of difluorine in the gas phase is far easier than heterolysis



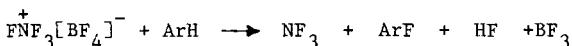
and reactions of difluorine above room temperature tend to be radical ones. For the latter to occur the homolysis can be suppressed by lowering the temperature, increasing the dilution, and adding radical scavengers. More importantly by stabilizing either one or both of the ions the process [1] could lead to heterolysis




where D and A are donor and acceptor molecules respectively, such as Lewis bases and acids. After interaction the formal positive charge on fluorine would be reduced by the electron flow indicated. It is interesting to note that quantum calculations indeed show that in triatomic cations containing fluorine the computed charge on fluorine is close to zero whether the fluorine is central or terminal [3]. One example of this type of stabilization is the formation of tetrafluoroammonium salts



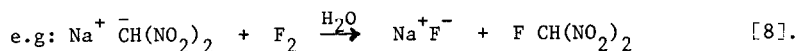
A fluoride ion is abstracted in the usual manner with a comparatively strong Lewis acid leaving an electron deficient fluorine to be stabilized by a very weak Lewis base. (If the base were strong it would interact directly with the acid without polarization of difluorine.) Similarly, salts are formed from difluorine and base-acid pairs such as Xe - SbF₅ and presumably would form from Ar₃P - SbF₅ or Ar₂S - SbF₅ combinations where Ar is an o and p substituted aryl group. The presence of positive fluorine can be inferred since NF₄⁺, and XeF⁺ salts, behave as electrophilic reagents in aromatic substitution reactions [4,5]



Stabilization of polarized difluorine with pyridine is also indicated by their adduct which can electrophilically substitute uracil at the 5 position [6]. The polarization would not proceed as far as in pyridine - iodine adducts when pyI⁺ and pyI⁺py ions are generated. Even the weak base benzene forms at least a transient π-adduct in which difluorine must be polarized  → F - F in order to explain the pattern of substitution [7]. This work is the most quantitative study so far and is effectively fluorination at 'infinite' dilution, with low

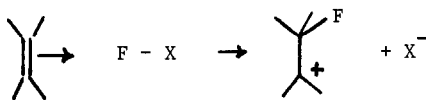
concentrations of aromatics, fluorinated diluents, F_2 /substrate ratios and conversions. Radical reactions are minimized by working at temperatures down to -154°C in the dark. The relative reactivities of substituted benzenes compared with benzene, and the isomer distributions, are typical of results expected for electrophilic substitution but with F_2 less selective than Cl_2 or Br_2 .

The other type of evidence for positive fluorine is the selective substitution at acidic hydrogens or at olefinic centres.



In this simple reaction (75-80% yield) if half the fluorine becomes fluoride then by a simple charge-balance the other half must be positive fluorine.

With olefins the same π -electron interaction as with an aromatic delocalized system is postulated to stabilize a fluoro-cation intermediate [9].



where X can be an oxy-chloro or a perfluorinated fluoroxy group.

Fluorine substitutes at the more nucleophilic end of the olefin indicating its positive nature. These reactions carried out at low temperatures, are unaffected by radical scavengers and hence cannot be fluorine atom reactions.

Christe's main evidence against positive fluorine is the direction of addition of fluorine perchlorate to a perfluoro-olefin. These olefins however are deactivated to electrophilic substitution especially at the low temperature (-45°C) used in his experiments. Their characteristic reactivity is towards nucleophiles as Miller demonstrated [10] and the direction of addition is governed by the stability of the intermediate fluoro-carbanion i.e. with perfluoropropene, $\text{CF}_3\text{CFCF}_2\text{Nu}^-$ would be

preferred over $\text{CF}_3\text{CF}(\text{Nu})\overset{-}{\text{CF}}_2$ and there would be no steric hindrance from the terminal CF_3 to attack by either possible nucleophile in the rate-determining formation of the former carbanion. The experimental result taken at face value shows twice as much addition with the polarization $\delta^+ \quad \delta^- \quad \delta^- \quad \delta^+$ F ClO_4 as with F ClO_4 . It certainly does not disprove the participation of any positive fluorine; possibly the oxidised products of the reaction may participate and affect the product ratio. Unequivocal demonstration of positive fluorine requires a substrate susceptible to electrophilic attack

Christe's other argument against positive fluorine is based on electronegativity, i.e. fluorine, the most electronegative element, can never show a positive polarity when combined with any other group.

This was partly dealt with in our previous paper in which we quoted some effects which run counter to the electro-negativity order of the halogens. We did not quote them as proof of positive fluorine merely as an indication that electronegativity arguments need to be used with restraint especially when discussing reactivity of molecules with small electronegativity differences. Thus with cyanogen halides the reactions of $(\text{NC})\text{Cl}$ show it behaves as a chloride, $(\text{NC})\text{I}$ behaves as a cyanide, whereas $(\text{NC})\text{Br}$ can react with either polarity [11], a fact not always appreciated by authors writing reaction mechanisms. Perchloryl fluoride can also react with different polarities. Under Friedel-Craft conditions the ClO_3 group can substitute benzene, but with donor solvents it can ring-fluorinate, e.g. 3,5-dimethoxyphenol in pyridine initially yields 2- and 4-fluoro-derivatives and 2-lithiothiophene in ether gives the 2-fluoro-thiophene.

One can argue that electronegativities measured from n.m.r. or Mössbauer spectra represent a static averaged picture of the electron distribution and that a small polarity within a molecule can be reversed when exposed to an asymmetric external charge distribution from reagents.

Some of our differences with Christe may only be semantic ones. He recognizes NF_4^+ as an electrophilic fluorinating agent [4] but not as a stabilized positive fluorine; we recognize that F^+ with a higher electron affinity than H^+ , is not a stable entity under ordinary conditions and that a bare F^+ will no more appear than a bare proton. Both need stabilizing on nucleophilic substrates.

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