

POLARIZATION OF X-F BONDS

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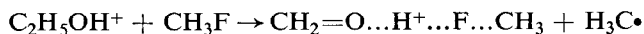
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SUMMARY

We discuss in this paper several reactions of compounds containing X-F (X = C, N, O, F, S and Xe) bonds. An attempt to unify these reactions conceptually is made by suggesting the importance of X-F bond polarization by protic media. Related Lewis-acid-induced polarization reactions can usually be envisioned. Some new reactions and mechanisms are suggested as a consequence of our analysis.

We discuss in this paper several reactions of compounds containing X-F (X = C, N, O, F, S and Xe) bonds and suggest that X-F bond polarization plays an important part in these reactions. Hydrogen bonds of the type F⁻...H...Y (Y = F, O or N) are among the strongest known^{1,2c} and the F⁻ ion can even be covalently bound and still form strong hydrogen bonds. For example, consider the following gas-phase C-C bond cleavage^{3d}:



We suggest that such polarization of covalent X-F bonds is a general, albeit not universal, phenomenon of fluorine chemistry.

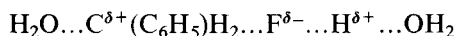
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^c This paper contrasts LiF...HF and HF...HF and other simple lithium, hydrogen and fluorine compounds.

^d One may compute that the cleavage of H₃C-CH₂OH⁺ to form H₃C• and CH₂OH⁺ is endothermic by approximately 30 kcal mole⁻¹ in the absence of CH₃F. The necessary thermodynamic data were taken from J. L. FRANKLIN, J. G. DILLARD, H. M. ROSENSTOCK, J. T. HERRON, K. DRAXL AND F. H. FIELD, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Positive Ions". *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.)*. No. 26, 1969.

Let us first consider the polarization of C-F bonds. Swain and Spalding have compared the hydrolysis of benzyl fluoride and benzyl chloride, and found only the former to be acid catalyzed⁴. (This difference in behavior appears to be a part of a general trend wherein heterolytic C-F bond cleavage is acid catalyzed but C-Cl, C-Br and C-I cleavage usually are not.) Whereas they explained their results in terms of direct polarization of the fluorine, Parker⁵ invoked the following C-F bond polarized intermediate:



Another example of C-F bond polarization is the hydrolysis of CF₂-containing cyclobutanes by hot concentrated H₂SO₄. For example, 1-phenyl-3,3-difluoro-, 2-R, 4-R', 4-R''-cyclobutenes hydrolyze to form the cyclobut-3-enone in approximately 90% yield for R = H, R' = R'' = Cl⁶; R = R' = Cl, R'' = H⁶; and R = F (or Cl), R' = R'' = H⁷. The reader may argue that this facile C-F bond cleavage is due to the high stability of the intermediate 1-phenylallylic (α -vinylbenzylic) carbonium ion. However, consider the reaction of the compound with the same framework as above but with R = H, R' = F, R'' = Cl. This yields the highly stable cyclobutene-dione by hydrolysis of the CFCl group⁸. The corresponding reaction of the related R = H, R' = R'' = Cl compound does not proceed; the CCl₂ group is not hydrolyzed. Not only is the above type of carbonium-ion stabilization impossible, but both of the above two cyclobutanones yield the *same* carbonium ion. Consider the acid hydrolysis of 1-phenyl-3,3-difluorocyclobutane to form benzalacetone⁶. We suggest the mechanism depicted below (see Fig. 1).

Temporarily leaving fluorocyclobutanes, the isomeric 5,5,6,6-tetrafluoro-1,3-cycloheptadiene and 6,6,7,7-tetrafluoro-1,4-cycloheptadiene hydrolyze to form 2-hydroxy-1-cycloheptatrienone (tropolone) in aqueous alkali or acetic acid under reflux when a little CH₃COOK and H₂O is added⁹. We believe the alkali is needed to remove HF from the tetrafluorocycloheptadienes to form 1,7,7-trifluoro-1,3,5-cycloheptatriene. KF is a sufficiently good base to react with HF to form solid KHF₂ and possibly some higher acid fluorides. However, it seems doubtful that KF alone could complete the rest of the hydrolysis to the tropolone, especially given the quantity used and the yields reported. We suggest C-F bond polarization by the protic CH₃COOH or H₂O and internal attack by the other oxygen of CH₃COOH or an oxygen of another H₂O molecule (see Fig. 2).

A second acetoxy group may be facily introduced in this manner. Admittedly, we can not exclude from consideration the possibility of a C-F-polarized intermediate forming a relatively free difluoro- or fluoro-hydroxy-tropylium ion, *e.g.*:



Finally, before turning to the thermochemistry of a model system, let us consider the aqueous or acid hydrolyses of 1,2-diethoxy-3,3,4,4-tetrafluorocyclo-

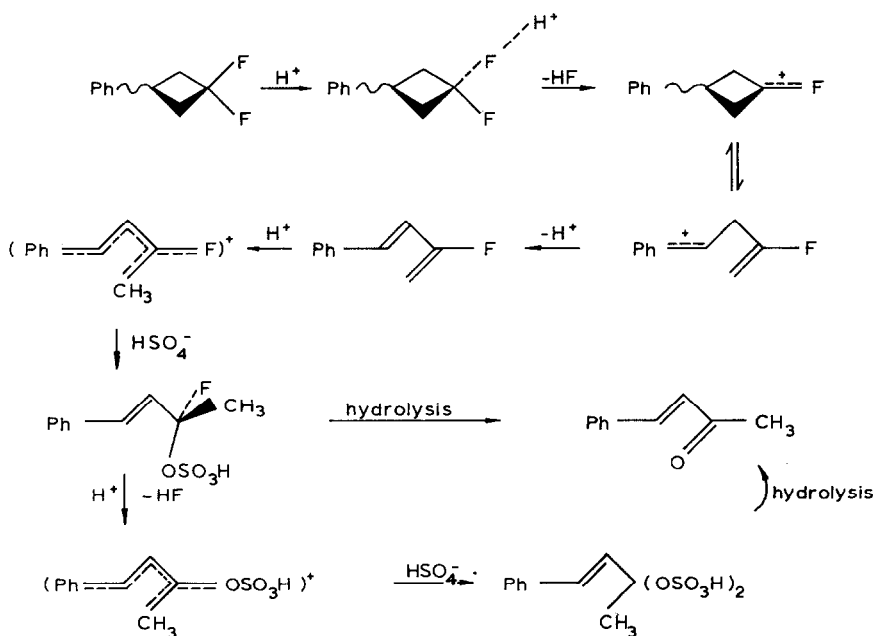


Fig. 1. Reaction of 1-phenyl-3,3-difluorocyclobutane with acid to form benzalacetone.

butene and 1-chloro-2,4,4-triethoxy-3,3-difluorocyclobutene to form 3,4-dihydroxycyclobutene-1,2-dione (squaric acid)¹⁰. It initially appears unlikely that the hydrolysis should proceed so readily in such high yield to such a highly "substituted" compound under such mild conditions as "aqueous". However, squaric acid is a highly stable compound *and* a very strong acid (pK_a comparable to H_2SO_4). We thus suggest that the hydrolysis is acid catalyzed in both cases and thus autocatalyzed in the former case.

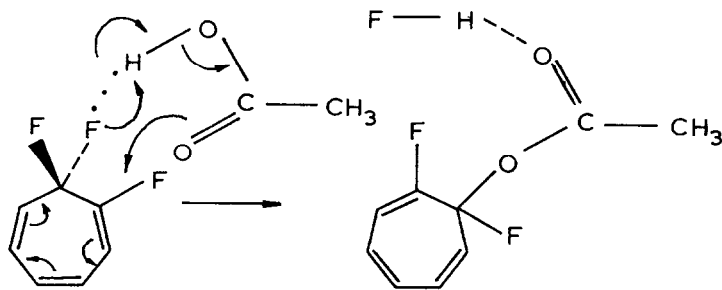
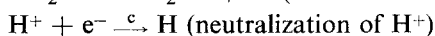
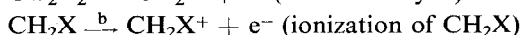
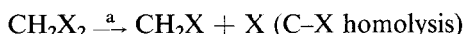


Fig. 2. Displacement reaction of 1,7,7-trifluorocycloheptatriene with acetic acid to yield 1,7-difluoro-7-acetoxycycloheptatriene.

It might be suggested that C-F bonds cleave more readily than C-Cl bonds simply because HF has greater stability than HCl [$D_e(\text{HF}) = 135 \text{ kcal mole}^{-1}$, $D_e(\text{HCl}) = 102 \text{ kcal mole}^{-1}$]¹¹ and because fluorocarbonium ions have higher stability than chlorocarbonium ions¹². However, we should also remember that C-F bonds are stronger than C-Cl bonds¹¹. In the absence of thermochemical data for the exact molecules of interest, let us examine the energetics of the two processes:



We will perform these reactions stepwise where X = F or Cl, using atomic and diatomic data from Ref. 11 and the rest from Lossing¹³.



The precise energies are given in Table 1.

TABLE 1

COMPARATIVE ENERGETICS FOR CH_2F^+ AND CH_2Cl^+ SYNTHESIS FROM THE DIHALOMETHANE

Process	Energy*, X = F	Energy*, X = Cl
a	120	76
b	205	203
c	-313	-313
d	-135	-102
Total	-123	-136

* All energies are in kcal mole⁻¹.

We may thus conclude that reaction (1) is 13 kcal mole⁻¹ less exothermic than (2) on thermodynamic grounds. It seems unlikely that the differences in the solvation energies for the hydrogen halides (*i.e.*, HF and HCl) and the halocarbonium ions (*e.g.*, CH_2F^+ and CH_2Cl^+) will be enough to compensate for the energy difference between CH_2F^+ (or any fluorocarbonium ion) and CH_2Cl^+ (or any chlorocarbonium ion). We conclude that the dominant factor must be that C-F bonds are more easily polarized than C-Cl bonds by protic media. This leads to the eventual displacement of HF by any nucleophile present.

Let us now turn to N-F bond polarization. Tertiary alkyl difluoramines $\text{R}_3\text{C-NF}_2$ (the three R groups need not be the same) readily lose F^- in acid^{14,15} and rearrange to form $\text{R}_2\text{C}=\text{N}^+(\text{F})-\text{R}$ ions. The difluorammonium ion ($\text{R}_3\text{C-NHF}_2^+$) is the most abundant protonated amine species; however, the transient

$R_3C-N(F)-F^+-H$ can also be formed. Rearrangement of this latter ion to yield $R_2C=N^+(F)-R$ accompanies increased N-F bond polarization by the proton, *i.e.*, we form a "full" H-F bond. Another example of the importance of polarization is in the reaction of N_2F_4 with $H_2C=C(CH_3)COOH$ to yield $CH_3C(CN)=NF$. Freeman¹⁶ cites this reaction and his mechanism is given in Figure 3.

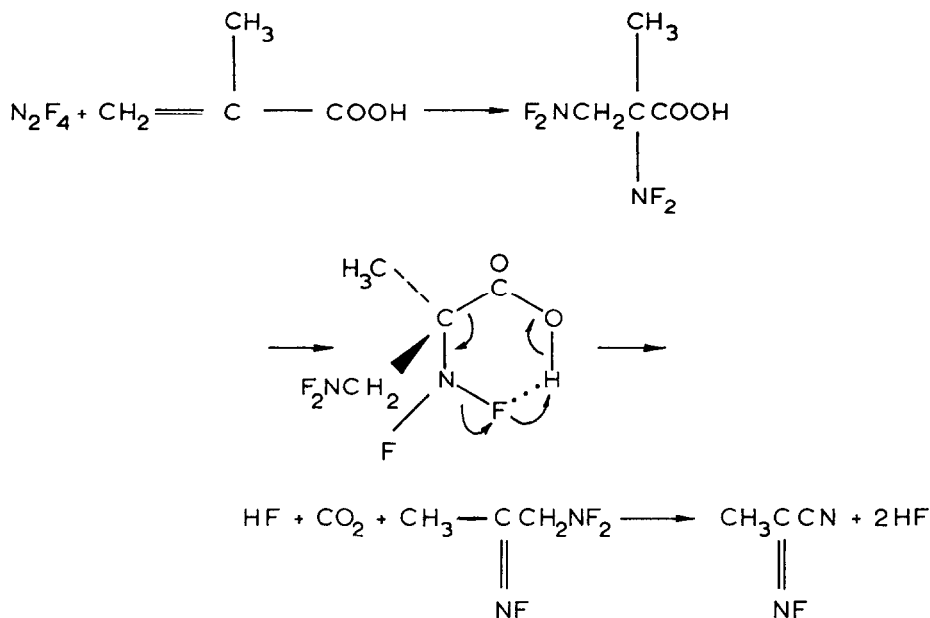
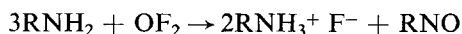


Fig. 3. Freeman's mechanism for the reaction of N_2F_4 with $H_2C=C(CH_3)COOH$ to form $CH_3C(=NF)CN$ (Ref. 16).

The reader will note the intramolecular N-F bond polarization by the carboxylic acid proton.

Consider O-F bond polarization. There are no direct data on the lack of reactivity. The reaction of OF_2 with the Lewis acids SbF_5 and AsF_5 to yield OF^+ is unobserved. Under high temperature and pressure (*e.g.*, 200°, 200 atm, 6 days), O_2^+ salts are formed while under more moderate conditions there is no reaction¹⁷. While OF^+ is the natural intermediate, it would have to be formed in the excited 1Δ state^{18*,19}. The high energy required is disadvantageous for synthesis of OF^+ salts. However, because X-OF is a singlet, its synthesis is facilitated.

Merritt and Ruff²⁰ report the following reaction:



We believe that their intermediate $RNH_2 \dots OF_2$ (see Fig. 4)

* This paper extrapolates the quantum chemical calculations of P. A. G. O'HARE AND A. C. WAHL, *J. Chem. Phys.*, 53 (1970) 2469.

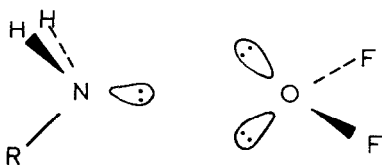


Fig. 4. Merritt and Ruff's intermediate in the reaction of RNH_2 with OF_2 to yield RNO .

is not likely owing to high lone-pair repulsion. This would tend to offset the small dipole-dipole attraction, as the dipole moment of OF_2 is only 0.3 D^{21} . Instead, we postulate hydrogen-bond-induced polarization of OF_2 by the amine, or preferably by RNH_3^+ (see Fig. 5).

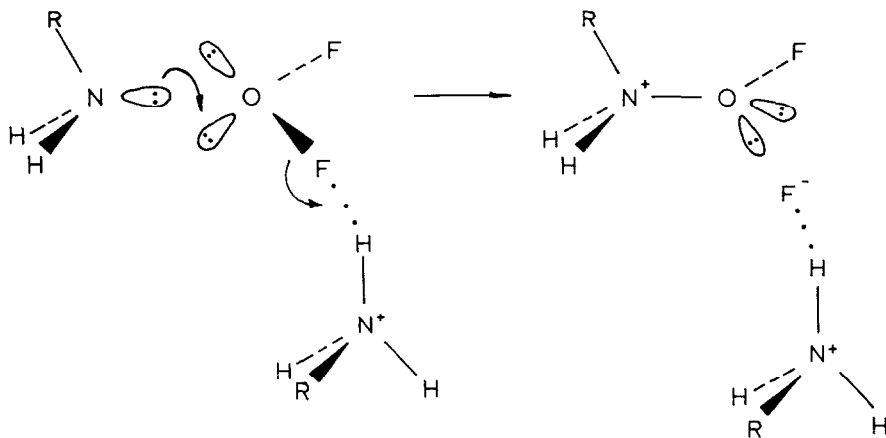
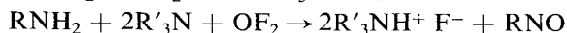
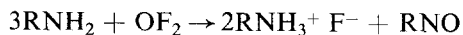


Fig. 5. The authors' preferred intermediate involving catalysis by RNH_3^+ .

This would result in increasing the partial positive charge on the oxygen, although it is probably improper to refer to the proposed complex as a stabilized ${}^1\Delta \text{OF}^+$ ion. The attack by the nucleophilic nitrogen of the first amine would be aided by the greater dipole-dipole attraction. In addition, the lone pairs on the oxygen would be shrunk by the increased effective nuclear charge on the oxygen. Our intermediate RNH_2OF^+ easily loses H^+ and HF to form RNO . We suggest that the addition of two moles of tertiary amine would serve to increase the yield of RNO by trapping the HF . (Compare the balanced reactions:



To prevent attack on the nitrogen of the tertiary amine, hindered bases such as 2,6-disubstituted pyridines should be used, though not so hindered that R_3NH^+ cannot catalyze the desired reaction.) Strong aqueous base readily decomposes OF_2 , accounting for the high pOH dependence of OF_2 synthesis from F_2 and NaOH in water²². We suggest a water-catalyzed reaction involving O-F bond polarization (see Fig. 6).

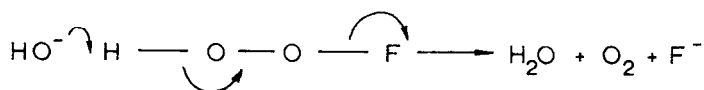
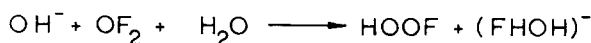
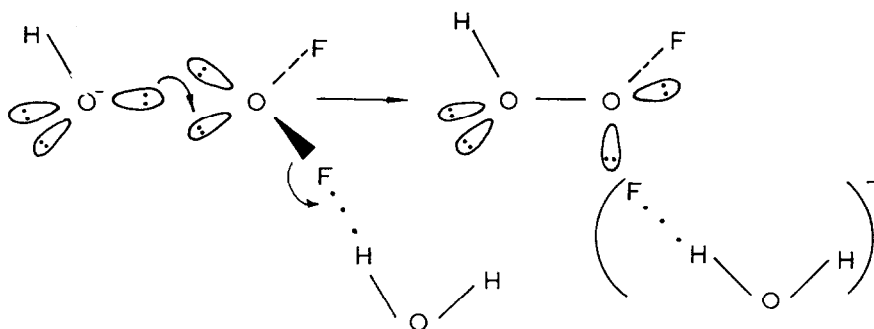


Fig. 6. Proposed mechanism of the base hydrolysis of OF_2 .

Attack on the fluorine atoms in OF_2 is unlikely because they are relatively negative and there would be excessive lone-pair repulsion (three lone pairs per F interacting with three lone pairs on OH^-). Likewise, we feel an unassisted $\text{S}_{\text{N}}2$ reaction on the oxygen would also be hindered by lone-pair repulsion.

Only indirect evidence is available on F-F bond polarization. Direct *cis*-fluorination of olefins has been accomplished at low temperatures in dilute CFCl_3 solution²³. The most logical intermediate is a 4-centered olefin-fluorine complex. In contrast, methoxy-substituted and rearranged products result if CH_3OH is used instead of CFCl_3 as the solvent. We postulate an intermediate involving hydrogen-bond-induced polarization of the fluorine molecule (see Fig. 7).

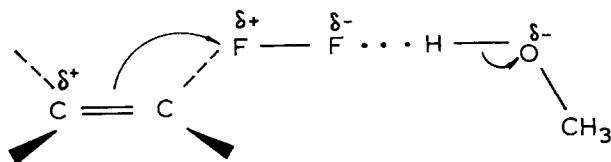
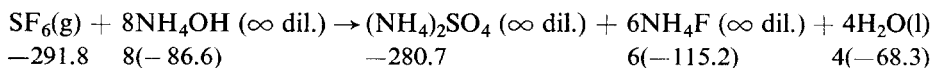


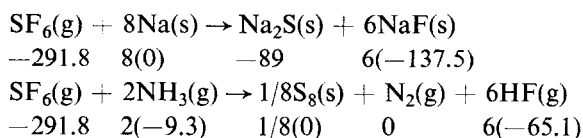
Fig. 7. Intermediate of the olefin fluorination by F_2 in methanol.

Let us now consider S-F bond polarization with regard to the chemistry of SF_6 . The modifications required for application to RSF_5 and R_2SF_4 derivatives

should be readily apparent to the reader. SF_6 is one of the most kinetically inert molecules²⁴, yet one would have expected the opposite from thermodynamic considerations. Consider the following hydrolysis reaction of SF_6 . The ΔH_f° value in kcal mole⁻¹ for each compound^{25,26} is given beneath its formula:



The net exothermicity of this reaction is 259 kcal mole⁻¹: the absolute magnitude changes with the precise hydrolysis condition but always appears to be highly exothermic. Sulfur hexafluoride is surprisingly stable to most reducing agents in addition to being surprisingly resistant to hydrolysis. Consider the following reactions and accompanying thermochemistry^{25,26}:



These reactions are exothermic by 622 and 80 kcal mole⁻¹ respectively. The first value is so phenomenal that we must ask if the observed slow reaction below 200° of Na and SF_6 ^{24,27} is due to the passivation of the Na surface by NaF. (Note, the melting point of Na is 98°.) Even this is surprising in that we would have thought the reaction was sufficiently exothermic to disrupt any neighboring passivated surface thereby allowing further reaction.

There are several semi-intuitive reasons why SF_6 is so inert in contrast to SF_4 ²⁸:

(1) The highly positive sulfur is shielded by six highly negative fluorines. This makes attack by any nucleophile, including the electron, extremely difficult.

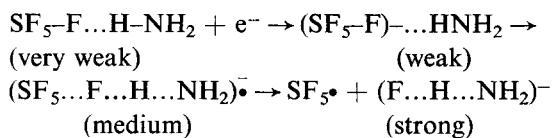
(2) SF_6 contains an octahedrally-coordinated sulfur. In contrast, SF_4 is pseudo-5-coordinated. In general, 6-coordination is preferred over 5- or 7- thereby making the $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ reactions more difficult. 4-Coordination is also "favorable" as manifest by the hydrolysis of SF_4 to SOF_2 ²⁸, a pseudo-4-coordinated molecule.

(3) The smallest non-vanishing electric multipole moment of a neutral charge array with strict octahedral symmetry, *i.e.*, $O_h A^{6\delta+}(B^{\delta-})_6$, is the hexadecapole moment. (In contrast, SF_4 has a dipole moment of 0.63 D²¹.) This implies that the long-range interactions between SF_6 and anything else will be very weak. Most reactions will thus have a low cross-section and thus a low reaction rate. Analogous reasons explain the kinetic stability of perchlorates, though in their case the lowest non-vanishing multipole moment after the monopole is the octopole.

The nucleophilic reagent that would be expected to react most readily with SF_6 is *the electron*. The reaction $\text{SF}_6 + e^- \rightarrow \text{SF}_6^-$, is expected to be both thermodynamically and kinetically favored, although one complication is that ground-state SF_6^- is definitely not octahedral because of a Jahn-Teller distortion²⁹. The

most recent value³⁰ for the exothermicity of the reaction—the electron affinity, probably the vertical electron affinity, of SF₆—is 19 kcal mole⁻¹. Charge-transfer reactions of SF₆ have been observed both in solution and in the gas phase^{31*}. Should SF₆^{-•} be formed, it would be destroyed *via* the reaction SF₆^{-•} → SF₅ + F⁻ and SF₅ then being rapidly destroyed by the solvent and/or additional electrons. This initial reaction is at most endothermic by 18 kcal mole⁻¹: one does a Hess cycle using the experimental electron affinity of SF₆³⁰, the S-F bond energy (≤ 78 kcal mole⁻¹)¹¹ and the electron affinity of fluorine (3.448 eV = 79 kcal mole⁻¹)³². In addition, the solvation energy of F⁻ is most probably higher than that of SF₆^{-•}. Cleavage of SF₆ by sodium both in liquid NH₃ and in a low-temperature mixture of diphenyl and ethylene glycol dimethyl ether has been observed²⁴. However, the difference in rates is quite phenomenal. In the former solution, at -64° the reaction takes “a few minutes”. In the latter case, it took close to 15 h during which time the reactants warmed from -64° to -10°. If we assume the validity of the “folk rule” that states reaction rates double every 10°, the former reaction is intrinsically around 2000 times faster.

We can explain this difference in terms of S-F bond polarization. In both cases, SF₆^{-•} is formed by electron addition to SF₆. In a non-polarizing solvent such as ethylene glycol dimethyl ether, small, probably stabilizing distortions of SF₆^{-•} are probably unaffected by the solvent. Moreover, large amplitude distortions are probably “discouraged” because of the intrinsic solvent “viscosity”. (This corresponds to the microscopic energy of moving solvent molecules.) In ammonia, both distortions are more facile since NH₃ is a small molecule. More importantly, one can write the following reaction (the adjectives give the strength of the hydrogen bond):



(Analogous NH₃-assisted reactions can be written for SF₅, SF₅⁻ and other lower valency S-F compounds.) In other words, the H in NH₃ serves to polarize the S-F bond in SF₆^{-•} and related species. An interesting test of this mechanism would be a comparison of the behavior of Na in the isomeric and isoelectronic solvents (CH₃)₃N and (CH₃)₂CHNH₂ or in the isoelectronic solvents CH₃OCH₂CH₂OCH₃ (the diphenyl is probably unnecessary) and CH₃NHCH₂CH₂NHCH₃. In both cases, solution of Na in the latter compound of the pair is predicted to provide the better reducing agent.

The corresponding reaction of SF₆ and aqueous electrons has been reported³³, the electrons being generated by pulse radiolysis. These authors, however, did not

* Hammond used ((CH₃)₂N)₂C=C(N(CH₃)₂)₂ as the electron donor for his solution research.

concern themselves with the dependence of the rate of reaction on pH other than to say $\text{SF}_6 + e^-$ "rapidly gives" $\text{SF}_5 + \text{F}^-$. However, they did study the rate of hydrolysis of SF_4 in both acidic and basic media. This reaction is catalyzed by both acid and base, though not surprisingly the rate is faster for the latter. To explain the acid hydrolysis, they invoked a hydrogen bond between H_3O^+ and the sulfur lone pair in SF_4 . It is hard to see why this would weaken the S–F bond. We agree with their suggestion of a hydrogen bond but instead offer an $\text{F}_3\text{S}\dots\text{F}\dots\text{H}\dots\text{OH}_2^+$ intermediate. This S–F-polarized intermediate might fragment to form H_2O , HF and the quite easily hydrolyzed SF_3^+ ion. Alternatively, the polarized intermediate may be directly attacked by a water molecule in an $\text{S}_{\text{N}}2$ -like manner forming the transient $\text{SF}_3\dots\text{OH}_2^+$. In any case, S–F bond polarization provides a simple explanation for the observed phenomena.

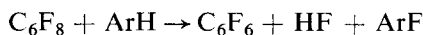
Another possible example of the importance of polarization in sulphur(IV)–fluorine chemistry involves the hydrolysis of trifluoromethyl perfluoroalkyl sulfur difluorides to the sulfoxide³⁴. When the sulfur(IV) difluorides are pure and in the absence of acid, they do not react with water or borosilicate glass. (However, when HCl is added, or the sulfur(IV) difluorides are impure and therefore probably contain HF, hydrolysis is rapid.) For the HCl reaction, Sauer and Shreeve³⁴ invoke the intermediacy of the sulfur(IV) dichloride. We feel this is unnecessary and instead suggest that the hydrolysis proceeds through S–F-polarized $(\text{R}_f)_2\text{S}(\text{F})\dots\text{F}\dots\text{HX}$ ($\text{X} = \text{F}$ or Cl) intermediates.

We now turn to Xe–F bond polarization. XeF_2 is known to react with Lewis acids to form stable complexes, although there is controversy over whether these should be described as XeF^+ salts³⁵ or as covalently bridged Xe–F-polarized adducts³⁶. Turning now to the "organic chemistry" of XeF_2 , XeF_2 is known to fluorinate arenes in both the gas phase³⁷ and in solution^{38–41}. Not surprisingly, the gas-phase reaction proceeds through a free-radical mechanism. The reactions in solution proceed through both radical and electrophilic substitution on the benzene ring. The latter is autocatalytic in the presence of a small amount of HF to form "a complex containing XeF_2 , HF and $\text{C}_6\text{H}_5\text{R}$ "⁴¹. This complex then decomposes to form the desired fluorarene or an arene radical that oligomerizes. In accord with this and conductometric and spectroscopic measurements of XeF_2 and XeF_2 in HF solution, an initial complex $\text{F}-\text{Xe}^{\delta+}\dots(\text{F}\dots\text{H}\dots\text{F})^{\delta-}$, *i.e.* a HF-polarized Xe–F bond, must be invoked. Unlike HF, HCl^{41,42} does not promote the reaction of XeF_2 and arenes in accord with the intuitive feeling that it is less able to polarize the Xe–F bond. The kinetic stability of XeF_2 in H_2O ⁴³ and NH_3 ⁴⁵ likewise suggests these hydrides are less effective than HF in bond polarization*.

There is usually insufficient data to predict with certainty the degree, or even occurrence, of X–F bond polarization. We know that 1,2,3,3,4,5,6,6-octafluoro-

* The half-life of XeF_2 in neutral H_2O at 0° is 7 h⁴³. Correspondingly, at least 97% of XeF_2 in H_2O is undissociated⁴⁴.

1,4-cyclohexadiene reacts with SbF_5 to form heptafluorobenzenonium hexafluoroantimonate⁴⁶. It is unlikely that HF will react with the cyclohexadiene to form an isolable HF_2^- salt. However, we predict extensive C-F bond polarization will occur and, by further analogy to XeF_2 , the following reaction is suggested:



This fluorination reaction, again like the one with XeF_2 , is predicted to be autocatalytic once a trace of HF is added. We recommend C_6F_6 as the solvent and as precursor for the C_6F_8 .

In conclusion, the polarization of X-F bonds ($\text{X} = \text{C}, \text{N}, \text{O}, \text{F}, \text{S}$ and Xe) by protic reagents is suggested as a general phenomenon of fluorine chemistry.

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