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CATALYTIC AND AUTOCATALYTIC DISPROPORTIONATION REACTIONS OF
FLUOROPHOSPHINES AND RELATED LOWER VALENCE NONMETAL FLUORIDES

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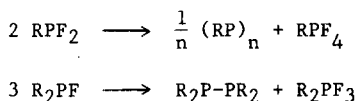
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SUMMARY

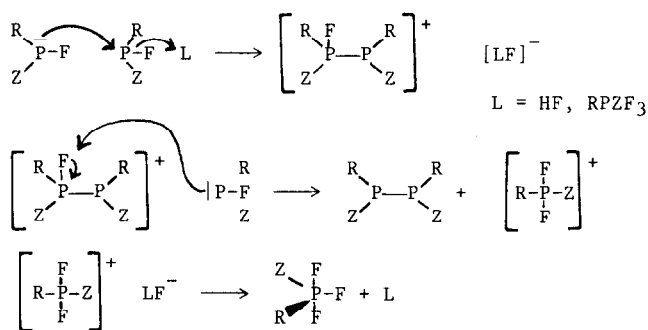
In this paper we discuss the mechanism of the related disproportionation reactions



We consider displacement reactions on both fluorine and phosphorus, catalysis and autocatalysis by hydrogen fluoride and the product fluorophosphorane, the effect of substituents on the rate, and iso-electronic analogies involving both other group V atoms and halogens. We also consider related disproportionation reactions of lower valence fluorides of other nonmetals such as S, Cl and Xe. From these comparisons, we deduce the following mechanism (Z = R,F)

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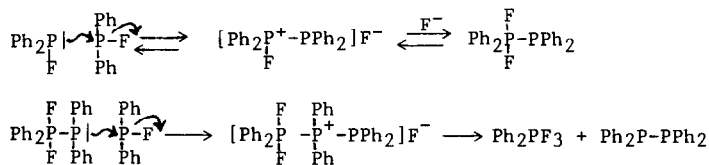
INTRODUCTION: LITERATURE MECHANISM AND THE ROLE OF ACID CATALYSIS

It is well established that fluorophosphines have a tendency to disproportionate into fluorophosphoranes and compounds containing P-P bonds [1,2]:



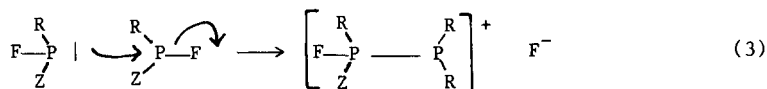
One observed regularity in this reaction is that it is slowed down by electronegative substituents [3,4]. For example, methyl difluorophosphine disproportionates considerably faster than the phenyl analog [5]. Analogously, to convert PF_3 into PF_5 and elemental phosphorus, it is necessary to use an electric discharge [6]. Alternatively, high temperature reaction of PF_3 with KF or CsF [7,8] may be employed where the high stability of the PF_6^- ion [9] assists the disproportionation. Furthermore, although perhaps not surprisingly, trialkyl phosphines show no tendency to disproportionate. In this paper we wish to discuss the mechanism of reactions (1) and (2) in the light of more general nonmetal chemistry.

Earlier [10] the following mechanism for the disproportionation of diphenyl fluorophosphine has been proposed (Scheme 1)



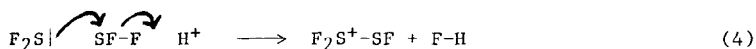
Scheme 1

An analogous mechanism can be written for other fluorophosphines and we commence our discussion with the initial formation of phosphino-phosphonium salts ($Z = F$ or R)

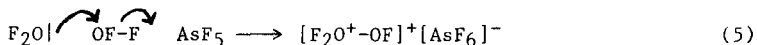


As a precedent we cite the formation of amino-, phosphino-, or arsino-phosphonium salts from the reaction of the chloro-amine, -phosphine or -arsine with alkyl phosphines [11,12]. In addition, of course, there is the well known quaternization reaction of tertiary phosphines with alkyl halides [13]. It is to be noted that alkyl fluorides are relatively inert in such nucleophilic displacement on carbon reactions [14], and in general, C-F [15], N-F [16], O-F [17,18], P-F [e.g. in PF_3] [19], S-F [20] and Xe-F [21] bonds are remarkably unreactive with regard to hydrolysis. Accordingly, we may thus explain the relative reactivities of the fluorophosphines. For the reaction of interest, it is necessary that the phosphine is both a good Lewis base [22] and a poor fluoride donor [23]. We expect analogous behavior for other fluorophosphines with electronegative substituents. Indeed, it is somewhat surprising that the disproportionation reactions occur as rapidly as they do [1]. By analogy to numerous other X-F ($X = \text{C}, \text{N}, \text{O}, \text{P}, \text{S}, \text{Xe}$) species [15-21], we anticipate catalysis by some Lewis or Brønsted acids [24]. Even if one discounts the possibility of HF formation by hydrolysis [25], the final fluorophosphorane serves admirably in this capacity [26]. While one hesitates to invoke catalysis by the product, some striking examples of autocatalysis [24] in C-F [27], S-F [28] and Xe-F [29] chemistry have been noted. We additionally note that acid-induced dimerization of SF_2 [30]*, formation of O_2^+ salts from OF_2 with AsF_5 [32,33], and formation of Cl_2F^+ salts from ClF and AsF_5 [34,35] have a mechanism related to (3),

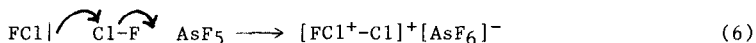
*In the meantime it has been reported that SF_2 and F_3SSF (recently isolated in especially high purity) do not disproportionate into SF_4 and S_2F_2 but decompose smoothly into SF_4 and elemental sulfur [31]. It cannot, however, be excluded that the amount of HF present in the system will affect the course of the disproportionation reaction of F_3SSF .



$\text{F}_2\text{S}^+-\text{SF}$ then acquires another F^- to form $\text{F}_3\text{S}-\text{SF}$



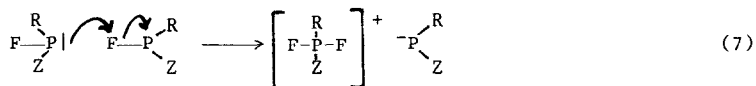
$\text{F}_2\text{O}^+-\text{OF}$ sequentially loses fluorine to form O_2F^+ , and then O_2^+



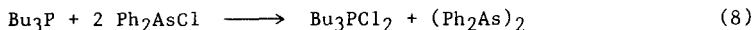
this salt can be isolated

As we do not expect corresponding transfer of carbanions [36-38], trialkyl phosphines are not expected to disproportionate nor do alkyl ethers, thioethers and halides react with acids to yield products analogous to those of reactions (4) - (6).

Alternatively, there could have been nucleophilic displacement on fluorine [39],

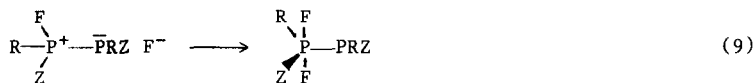


Although analogous reactions of phosphines and C-F [40], N-F [41], S-F [42] and Xe-F [43] bonds may be noted, in all cases there is a considerably better leaving group than PZR^- and/or a weaker X-F bond being broken. It is well known that fluorine simultaneously destabilizes adjacent anions [44] relative to, and is less susceptible to nucleophilic displacement reactions on halogen, than its congeners [39]. As such, this does not disqualify analogs of this reaction from occurring in the reaction of trialkyl phosphines with halo derivatives of the trivalent group V elements [11]. For example,



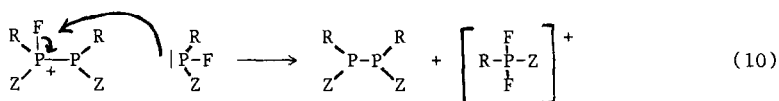
THE REACTION OF PHOSPHINOPHOSPHONIUM IONS WITH NUCLEOPHILES

Let us now consider the next step, the conversion of the phosphinophosphonium salt to the phosphinophosphorane



This step has numerous precedents: we know of both halophosphoranes and phosphonium halides [45] and indeed, a phosphinophosphorane has recently been isolated [46,47]. Indeed, we have earlier cited the

dimerization of SF₂ [30] as precedent and recall that the relative stability of pentacoordinate P, As and Sb has also been invoked to explain the (relative) ease of reactions such as (1), (2) and (8). Owing to the high P-F bond strength and the low F-F bond strength [48], we do not anticipate a nucleophilic attack on the P-F bond by F⁻ to form the diphosphine and F₂. (The analogous S_N2 reaction on iodine by I⁻ in the reaction of iodophosphines is much more reasonable and may be used to explain the absence of iodophosphoranes in the related disproportionation of iodophosphines [49]). We anticipate the equilibrium between the phosphinophosponium ion and phosphino-phosphorane to be set up quickly. However, there is a (probably) slow nucleophilic displacement reaction on fluorine that yields the diphosphine and a new phosphonium ion



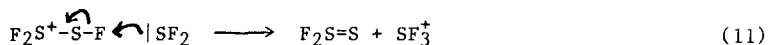
The RZPF₂⁺ ion then acquires an F⁻ ion to form the observed fluoro-phosphorane. We note at this juncture that if Z = F, it is clearly imperative that there be a further reaction to form the polymeric (RP)_n but all reactions described so far have formal analogues here. We have no way to date to differentiate between the proposed S_N2 (F) reaction and the phosphorano-phosphino-phosponium ion suggested earlier [10]. Most assuredly, analogues of the latter are necessary in the reaction of trialkyl phosphines with derivatives of the other trivalent group V elements [11,12].

RELATED DISPROPORTIONATION REACTIONS OF SF₂ AND ClF*

However, let us discuss precedents for reaction (10) as to perhaps make it more plausible. The first reaction returns us to the chemistry of SF₂ where it is additionally known that acid treatment of SF₂ and its dimer results in the formation of SF₄ and both S₂F₂ and S₈, depending

*We recognize ClF, SF₂, and PF₃ as a set of perfluorinated 'equivalent elements' or 'paraelements' [50] as are F₂S⁺-SF and FCl⁺-Cl. These fluorocations are also related to the above phosphinophosponium ions by 'paraelement' and isoelectronic reasoning.

on the conditions [30,31]. To explain the formation of SF_4 and S_2F_2 , it is merely necessary to invoke reaction (11) or analogous reactions



to yield F-S-S-F by attack on the other fluorines. (We also anticipate related reactions with F_3S^+-S [25] although we will not attempt to predict the relative rates of the three S_N2 (F) reactions). The SF_3^+ ion will then pick up an F^- ion to form SF_4 in an equilibrium reaction between the sulfurane and sulfonium ion, analogous to the above phosphorane-phosphonium ion problem. To form elemental sulfur, one need only invoke the intermediacy of S_2F^+ . (This is a well-characterized ion [30] that should readily be formed by F-transfer from S_2F_2 to SF_3^+ , reaction (12)).



This ion can then react with F_2S-S to form F_2S (to be recycled) and S_3F^+ through the intermediacy of $F_2S^+-S_3-F$. Subsequent chain lengthening yields S_n^+-F and eventually a ring fluorinated cyclo-sulfur cation [51]. In the presence of a very good fluoride acceptor, the ring fluorinated cyclo-sulfur cation is transformed into a ring dication, as observed in this reaction and more definitively by the oxidation [52] of preformed cyclooctasulfur [53]. Otherwise this fluorinated cyclo-sulfur cation can react with SF_2 , $FSSF$ or F_2SS to form S_8 and SF_3^+ , F_2SSF^+ or $(F_3SS)^+$.

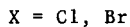
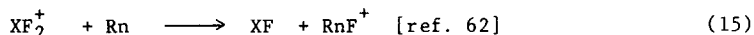
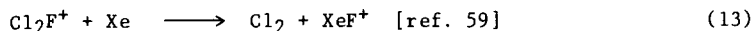
We note that the analogous disproportionation reactions of CF_3SF or its dimer [54] stop at CF_3SF_3 and CF_3SSCF_3 , a finding compatible with the instability and lack of 'transferability' of CF_3^- in contrast to F^- .

Another precedent for reaction (10) is the formation of ClF by the spontaneous reaction [55] of Cl_2 and ClF_3 , and the related decomposition of Cl_2F^+ to form Cl_2 and ClF_2^+ [34,35], recalling that we have already mentioned the formation of Cl_2F^+ from ClF and a strong Lewis acid. Transferring fluorine from Cl_2F^+ to another molecule of ClF yields ClF_2^+ and Cl_2 , while the analogous S_N2 (Cl) reaction with Cl_2 gives Cl_3^+ salts. These are unstable and so Cl_2 is observed.

The reaction of Cl_2 and ClF_3 is analogous to that just given but "with the film run backwards". If there is not a suitably strong fluoride acceptor, we must consider the products formed by reaction of Cl_2F^+ and ClF_2^+ with F^- . In the former case, attack on the terminal chlorine occurs to form 2 ClF (ClClF_2 is seemingly unstable) while in the latter case ClF_3 (FClF_2) is formed. Accordingly, the direction of the reaction is dependent solely on the relative stabilities of the ions Cl_2F^+ and ClF_2^+ , and the neutral Cl_2 , ClF and ClF_3 [56-58].

RELATED NUCLEOPHILIC DISPLACEMENT REACTIONS ON FLUORINE

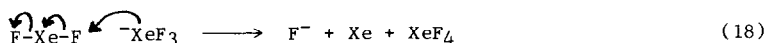
For completeness, we now list some other related nucleophilic displacement reactions on fluorine involving cationic donors of fluorine, the so-called 'type 3' $\text{S}_{\text{N}}2$ (F) reactions [39].



There are many other reactions that are also probably of this type such as the disproportionation reactions of the other halogen fluorides [63]. In this regard, numerous possible reactions are impeded by either the low base strength of the nucleophile and/or the weak F^- donating ability as earlier noted for the lack of disproportionation reaction of PF_3 . Such examples include the non-equilibration of the xenon fluorides with xenon. For example, while thermochemical data [64] are insufficient to decide on whether reactions (16) and (17) are exothermic or endothermic,



we know of no low temperature equilibrium reaction [65]. No reaction of Xe with XeF_3^+ is known to the authors. This may be understood in terms of relative instability of XeF_3^+ [66,67]. However, XeF_4 is seemingly too poor a base to react with XeF_3^+ to form XeF_2 and XeF_5^+ and so to catalyze reaction (17). Indeed, XeF_2 and XeF_5^+ salts form stable complexes in the solid [68]. In principle, one could also accomplish reaction (16) by an anionic $\text{S}_{\text{N}}2$ (F) reaction (18) but the necessary



XeF_3^- does not appear to be stable in solution [69]. We recall PF_3 does not disproportionate or equilibrate with PF_5 and elemental phosphorus. That this may be accomplished by heating with alkali metal fluorides [7,8] suggests that one may likewise disproportionate or equilibrate the xenon fluorides. We know of no such study in this regard.

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