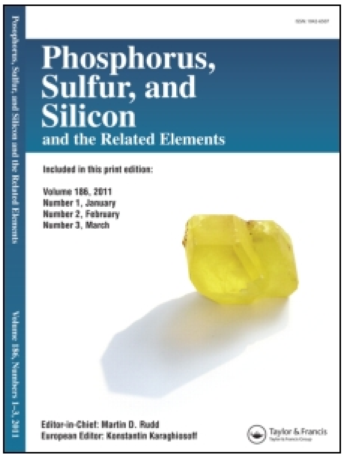


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

On the Nucleophilic Degradation of Phosphorus Chalco-Genides with Adamantane-Like Structure by Fluorides

M. Meisel[a]
[a] Zentralinstitut für anorganische Chemie der Akademie der Wissenschaften der DDR, Berlin

To cite this Article Meisel, M.(1990) 'On the Nucleophilic Degradation of Phosphorus Chalco-Genides with Adamantane-Like Structure by Fluorides', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 137 — 140
To link to this Article: DOI: 10.1080/10426509008040700
URL: http://dx.doi.org/10.1080/10426509008040700

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, pp. 137–140
Reprints available directly from the publisher
Photocopying permitted by license only

ON THE NUCLEOPHILIC DEGRADATION OF PHOSPHORUS CHALCOGENIDES WITH ADAMANTANE-LIKE STRUCTURE BY FLUORIDES

M. MEISEL

Zentralinstitut für anorganische Chemie der Akademie
der Wissenschaften der DDR, Rudower Chaussee 5,
Berlin 1199, DDR

Abstract Some new results, especially on the fluoride degradation of phosphorus sulfides and phosphorus oxide sulfide are reported. Possible reaction mechanisms are discussed.

In the same way as in reactions of other inorganic polymers there are two possibilities of the course of degradation reaction of the adamantane-like structures of the phosphorus chalcogenides:

- reorganization which causes change of constitution and structure of compounds in the reaction system without change of the gross composition of this system
- directed degradation yielding only some definite reaction products according to an easy to survey mechanism

It strongly depends on influences like temperature, reaction medium, physical and chemical properties of the primary formed products which of these possibilities is realized.

It is shown with the examples of the nucleophilic degradation of P_4O_{10}, $P_4O_4S_4$ and P_4S_{10} by the fluoride ion that both reaction types may occur in these systems.
As first was shown by H. Grunze and collaborators [1,2] in a typical reorganization process P_4O_{10} reacts with alkali and ammonium fluoride , respectively, forming mixtures of various fluorophosphates and phosphates. Depending on the cation and the molar ratio F:P representatives of up to four homologous polymeric phosphates could be identified in the reaction products:

$P_nO_{3n-1}F_2{}^{n-}$	difluoro polyphosphates
$P_nO_{3n}F^{(n+1)-}$	monofluoro polyphosphates
$P_nO_{3n+1}{}^{(n+2)-}$	polyphosphates
$P_nO_{3n}{}^{n-}$	cyclophosphates

Thus, the reaction of NH_4F and P_4O_{10} in the molar ratio of 4:1 does not lead to difluoro diphosphate according to

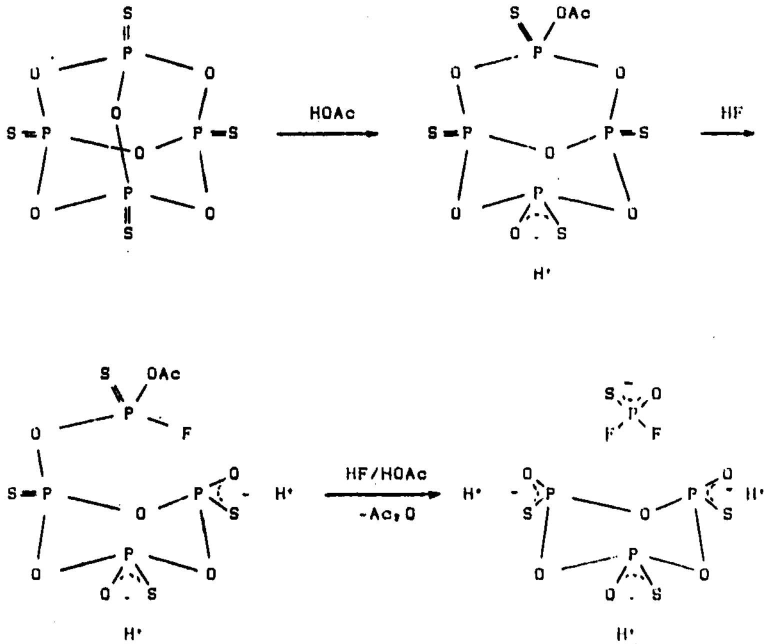
$$P_4O_{10} + 4\ MF \longrightarrow 2\ M_2[P_2O_5F_2] \qquad (M= NH_4,\ Li,\ Na,\ K) \qquad (1)$$

but to a mixture of difluorophosphates, monofluorophosphates and polyphosphates of the same gross composition.[1]

On tempering of the obtained glassy products under further reorganization some definite compounds can be enriched in these mixtures. In this way it is possible to isolate oligomeric difluorophosphates up to n=5 by fractionating crystallization.[2]

The reaction behaviour of sulfur-containing phosphorus adamantanes is quite different. So it is impossible to obtain fluoro monothiophophates by melting $P_4O_6S_4$ with fluorides because as a result of sulfur-oxygen ligand exchange in addition to the monothio derivatives sulfur-free and dithiophosphates are formed.

However, in glacial acetic acid as reaction medium $P_4O_6S_4$ will be degraded in definite steps.[3] As shown in the following Scheme the first step is the nucleophilic attack of the acetate ion at one phosphorus atom :



Under cleavage of one P-O-P bond a bicyclic acetyl thiophosphate is formed as primary product. This compound was identified by its ^{31}P-NMR spectrum of ABX_2 type. In presence of ammonium fluoride by further nucleophilic attack of F^- at the same P-atom the top of the $P_4O_6S_4$ cage is split off yielding difluoromonothiophosphate and trithio cyclotriphosphate as insoluble ammonium salt (see Scheme).

With potassium fluoride nearly independent of the molar ratio $KF:P_4O_6S_4$ monofluoro monothiophosphate has been obtained as main product, which is formed according to the simplified equation (2)

$$P_4O_6S_4 + 4\ F^- + 4\ OAc^- \longrightarrow 4\ SPO_2F^{2-} + 2\ Ac_2O \qquad (2)$$

The first step is probably the same as in the case of NH_4F degradation, but due to the different solubilities and to the different nucleophilic reactivity of acetate and fluoride in presence of KF the phosphorus oxide sulfide presumably reacts completely to a mixture of acetyl monothiophosphates:

$$P_4O_6S_4 + 6\ OAc^- \longrightarrow 2\ POS(OAc)_2^- + 2\ PO_2S(OAc)^{2-} \qquad (3)$$

As diacetylphosphate the diacetyl monothiophosphate likely is not stable in glacial acetic acid [4] and reacts to monoacetyl monothiophosphate and acetic anhydride:

$$POS(OAc)_2^- + HOAc \longrightarrow HO\overset{O}{P}S(OAc)^- + Ac_2O \qquad (4)$$

Finally monofluoro monothiophosphate may be formed by exchange of the acetyl group for fluoride.

The different nucleophilic reactivity of the alkali fluorides has been studied on the example of fluoridolysis of phosphorus (V) sulfide in acetonitrile at room temperature. The reactions were performed according to the following formal equations:

$$P_4S_{10} + 4\ F^- \longrightarrow 2\ P_2S_5F_2^{2-} \qquad (5)$$

$$P_4S_{10} + 6\ F^- \longrightarrow 2\ PS_2F_2^- + 2\ PS_3F^{2-} \qquad (6)$$

$$P_4S_{10} + 8\ F^- \longrightarrow 2\ PS_2F_2^- + 2\ S^{2-} \qquad (7)$$

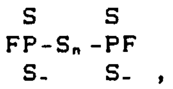
It was found that LiF does not react under these conditions. NaF reacts mainly according to equation (5) (80% $Na_2[P_2S_5F_2]$, 10% $Na[PS_2F_2]$) whereas on the reaction of KF with P_4S_{10} only $K_2[P_2S_5F_2]$ is formed.

It is remarkable that under these conditions the reactivity of CsF is lower than that of NaF and KF respectively. One reason for that is the only slight solubility of the first obtained $Cs_2[P_2S_5F_2]$ which renders more difficult the further nucleophilic attack of fluoride.

On melting KHF_2 or NH_4HF_2, respectively, with P_4S_{10} in a molar ratio of 4:1 difluoro dithiophosphate is obtained in almost quantitative yields (equ.(8)).[5]

$$P_4S_{10} + 4\ MHF_2 \longrightarrow 4\ M[PS_2F_2] + 2\ H_2S \quad (M= K, NH_4) \quad (8)$$

The reaction of sulfur-rich phosphorus sulfides "P_4S_{10+n}" (n= 1 to 6) with fluoride in acetonitrile or 1,2-dimethoxyethane[4] leads to oligomeric sulfane-α,ω-diyl-bis(fluorodithiophosphates),



$$\begin{array}{c} S \qquad\quad S \\ FP\text{-}S_n\text{-}PF \\ S^- \qquad S^- \end{array}$$

(n= 1-8)

which are identified by ^{19}F and ^{31}P-NMR spectroscopy. The average chain length n of the sulfane derivates depends on the S:P ratio of the starting phosphorus sulfides.

These results may be explained by the assumption of a substitution of bridging S-atoms in the P_4S_{10} cage by S_n-units in the sulfur-rich phosphorus sulfides. However, difluoro pentathiodiphosphates react with sulfur in CH_3CN also to a mixture of oligomeric sulfane bis(fluorodithiophosphates). Therefore no definite conclusions about the molecular structure of the sulfur-rich phosphorus sulfides are possible from the nucleophilic degradation by fluoride.

In generalization of the results obtained some reaction mechanisms of the nucleophilic degradation of cage-like phosphorus chalcogenides by fluoride under different reaction conditions are discussed.

REFERENCES

1. H. Grunze and I. Grunze , Z. Naturforsch., 23b, 746 (1968); Bull. Soc. Chim. France, 1968, 1675
2. H. Grunze, J. Neels and I. Grunze, Z. anorg. allg. Chem., 400, 137 (1973)
3. G.-U. Wolf and M. Meisel, unpublished results
4. J. Neels and H. Grunze, Z. anorg. allg. Chem., 495, 65 (1982)
5. M. Meisel, unpublished
6. J. Neels, A.-R. Grimmer, M. Meisel, G.-U. Wolf, H. Jancke, Z. anorg. allg. Chem., 547, 83 (1987)