On the Reaction of Phosphorous Acid with Superacids and the Crystal Structure of $H_5O_2^+SbF_6^-$ and $Me_4N^+HPF_5^-$

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Phosphorous acid reacts with the superacidic system HF/SbF_5 with formation of HPF_4, water, and oxonium hexafluoroantimonate, which crystallizes as $H_5O_2^+SbF_6^-$ in the triclinic space group $P\bar{1}$ with $a = 6.492(6)$ Å, $b = 7.469(8)$ Å, $c = 8.095(6)$ Å, $\alpha = 116.17(7)°$, $\beta = 93.90(7)°$, and $\gamma = 112.34(7)°$, with two formula units per unit cell. The unit cell contains two $H_5O_2^+$ ions of approximate symmetry C_{2h} with an intramolecular O···O distance of 2.418(8) or 2.40(1) Å, respectively. The reaction is discussed with regard to the formation of protonated species in various superacidic media. In addition the crystal structure of $Me_4N^+HPF_5^-$ which is formed by the reaction of HPF_4 with $Me_4N^+F^-$ is reported. The salt crystallizes in the tetragonal space group $P4/nmm$ with $a = 8.564(5)$ Å and $c = 5.687(2)$ Å, with two formula units per unit cell. The P−F distances of $P-F_{eq} = 1.595(6)$ Å and $P-F_{ax} = 1.594(9)$ Å for the ψ-octahedral HPF_5^- show no significant interaction exercised by hydrogen on the *cis*- and *trans*-fluorine.

Introduction

The solutions of AsF_5 and SbF_5 in HF and FSO_3H, respectively, belong to the strongest acids.[1] The superacidic systems HF/MF_5 (M = As, Sb) have been used successfully for the protonation and isolation of very weak bases such as H_2O_2, H_2S_2, SeH_2, and SbH_3.[2−5] Besides the fact that HF/MF_5 are slightly stronger acids than FSO_3H/SbF_5, the superacidic HF systems were found to be more suitable for preparation and crystallization of the protonated species. This is largely due to the volatility of HF, which allows a convenient isolation of the products at dry ice temperature.

The use of the superacidic HF systems as powerful protonating agents for the preparation of a desired species is sometimes limited due to reactions between HF and the base. This is well-known for compounds containing silyl groups which are cleaved by HF. The driving force for this behavior is the thermodynamically favored formation of the Si−F bond (595 kJ/mol), which is the strongest known single bond after the B−F bond (646 kJ/mol). Phosphorus compounds exhibit in some cases a similar reactivity, since the P−F bond strength (496 kJ/mol) ranks in fourth place, after the H−F bond (565 kJ/mol).[6]

In the course of our studies of superacidic reactions, we have investigated the behavior of phosphoric acid in HF/MF_5 as an example of the above mentioned differences in reactivity. H_3PO_4 is known to form protonated species in the superacid FSO_3H/SbF_5.[7] Despite the fact that phosphoric acid undergoes fluorination in anhydrous HF (eq 1),[8] we found in previous experiments that the tetrahydroxyphosphonium salts are quantitatively formed in the superacidic media HF/MF_5 (eq 2).[9] Therefore we extended the investigation to the phosphorous acid which is known to yield HPF_4 in anhydrous HF.[10]

$$H_3PO_4 + HF \rightarrow H_2PO_3F + H_2O \tag{1}$$

$$H_3PO_4 + HF + MF_5 \rightarrow P(OH)_4{}^+MF_6{}^- \tag{2}$$

$$(M = As, Sb)$$

In addition we report the crystal structure of $Me_4N^+HPF_5^-$. The HPF_5^- anion is the only known main group element species containing five fluorine ligands and one hydrogen ligand, and it offers therefore an opportunity to study the mutual ligand interaction effects on fluorines in *cis* and *trans* positions.[11]

Experimental Section

All synthetic work and sample handling was performed by employing standard Schlenk techniques and a standard vacuum line (stainless steel or glass, respectively). H_3PO_3 (purum p.a., Fluka) was used without any further purification. SbF_5 (p. synth., Merck) was fractionally distilled. The syntheses of HPF_4[10] and Me_4NF[12] and the drying of HF[4] and CH_3CN[13] were carried out by known literature methods.

Infrared spectra were recorded on a Bruker ifs 113v spectrophotometer. Spectra of dry powders were obtained on a coated CsBr plate. The Raman spectra were recorded on a T64000 (ISA) using a CCD detector (EEV CCD15-11) and an Ar^+ laser (514.5 nm) from Spectra Physics. The spectra were recorded in a glass cell cooled with liquid

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nitrogen. The NMR spectra were recorded with a Bruker DPX 300 spectrometer. Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen, and an X-ray diffraction study was carried out using a Nicolet R3/mV automated diffractometer.

Reaction of Phosphorous Acid with HF/SbF$_5$ and Formation of $H_5O_2^+SbF_6^-$. In a 50 mL KEL-F reactor, 1.16 g (5.35 mmol) SbF$_5$ was dissolved in 2 g of HF. The solution was frozen at −196 °C, 0.43 g (5.35 mmol) H_3PO_3 was added under an inert atmosphere (N_2), and the mixture was warmed to −50 °C and kept for 2 h. No precipitation was observed. The excess of HF and the formed volatile materials were removed under dynamic vacuum at −78 °C. The remaining colorless solid was identified as $H_5O_2^+SbF_6^-$ by vibrational spectroscopy.[14−17] It contained crystals suitable for X-ray diffraction studies. Infrared spectral data for $H_5O_2^+SbF_6^-$ (cm^{-1}): 282 s, 666 vs, 1028 s (br), 1657 s, 3420 s (br).

Preparation of $Me_4N^+HPF_5^-$. A 190 mg (2 mmol) amount of Me$_4$NF was placed in a dried KEL-F reactor, and 2.6 g (24 mmol) of HPF$_4$ was condensed into the reactor at −196 °C. The frozen mixture was warmed to −40 °C and stirred for 2 h. The excess of HPF$_4$ was removed under dynamic vacuum. The colorless micro crystalline $Me_4N^+HPF_5^-$ was formed in quantitative yield, and its purity was checked by vibrational and NMR spectroscopy. The growing of suitable crystals for X-ray diffraction studies was achieved by ultrasonic treatment of the microcrystals suspended in dry acetonitrile for 1 day. Raman spectral data for $Me_4N^+HPF_5^-$ [cm^{-1} (relative intensity)]: 375 (9.6), 439 (1), 460 (4.5), 511 (1.7), 543 (1.3), 556 (0.7), 605 (5.6), 755 (36), 767 (10), 950 (27), 1176 (2.8), 1236 (5.1), 1289 (2.5), 1417 (4.0), 1471 (40), 1536 (1.7), 2353 (10.6), 2370 (11), 2485 (5.6), 2820 (12), 2889 (14), 2925 (39), 2965 (81), 2998 (64), 3043 (100).

Results and Discussion

Reaction of H_3PO_3 with HF/SbF$_5$. Phosphorous acid reacts with HF/SbF$_5$ with formation of HPF$_4$ (eq 3) at −50 °C. The fluorination of phosphorous acid proceeds fast under these conditions. NMR spectroscopic measurements at low temperature gave no indication of the formation of a trihydroxyphosphonium cation. Thus the fluorination of H_3PO_3 (eq 4) is not altered by the acidification of HF with SbF$_5$ as it was observed in the analogous case of H_3PO_4 (eq 2).[9]

$$H_3PO_3 + 5HF + SbF_5 \rightarrow HPF_4 + H_3O^+SbF_6^- + 2H_2O \quad (3)$$

$$H_3PO_3 + 4HF \rightarrow HPF_4 + 3H_2O \quad (4)$$

Since HPF$_4$ possesses no basic properties, reaction 4 serves as a water source for the superacidic system. The resulting mixture consists of oxonium hexafluoroantimonate with two water molecules dissolved in HF and the HPF$_4$. Following our regular procedure for removal of HF at dry ice temperature, we found $H_5O_2^+SbF_6^-$ as the remaining solid instead of the expected $H_7O_3^+SbF_6^-$. The $H_5O_2^+SbF_6^-$ was identified by infrared spectra. The H_3O^+, $H_5O_2^+$, and $H_7O_3^+$ cations show significant differences in the region of the O−H stretching modes.[14−17] At first, the removal of water from an assumed $H_7O_3^+$ SbF_6^- was surprising to us. Although HF is known to form an azeotrope with water, the dehydration was not expected at dry ice temperature. Therefore we repeated this procedure with $H_5O_2^+$ and found that it also undergoes dehydration, but several cycles are required to obtain pure $H_3O^+SbF_6^-$. Summarizing all observations on the above described experiments, we found that $H_5O_2^+SbF_6^-$ can be obtained by careful removal of HF. Species containing more water molecules were not found to be sufficiently stable to survive dehydration by HF.

Table 1. X-ray Diffraction Data of $H_5O_2^+SbF_6^-$ and $(CH_3)_4N^+HPF_5^-$

formula	$H_5F_6O_2Sb$	$C_4H_{13}F_5NP$
space group	$P\bar{1}$ (No. 2)	$P4/nmm$ (No. 129)
a, Å	6.492(6)	8.564(5)
b, Å	7.469(8)	
c, Å	8.095(6)	5.687(2)
α, deg	116.17(7)	
β, deg	93.90(7)	
γ, deg	112.34(7)	
V, Å^3	312.4(5)	417.1(4)
ρ_{calcd}, g cm^{-3}	2.900	1.601
Z	2	2
fw,	272.79	201.12
μ, mm^{-1}	4.479	0.355
temp, °C	−102(2)	−99(2)
λ, Å	0.710 69	0.710 69
R^a [$I > 2\sigma(I)$]	0.038	0.091
R^a (all data)	0.039	0.094

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. Refinement method: full-matrix least-squares calculations based on F^2.

Although the cations H_3O^+, $H_5O_2^+$, and $H_7O_3^+$ show different spectroscopic features, infrared spectra are ambiguous because of contamination of a sample by moisture during sample preparation and measurement. Therefore the above described observations were confirmed by X-ray diffraction studies. The crystal structure of oxonium hexafluoroantimonate was investigated by Christe et al. by powder X-ray and neutron diffraction.[18] Later, Larsen et al. determined the single-crystal structure.[19] Crystal structures of $H_5O_2^+SbF_6^-$ and higher hydrated oxonium hexafluoroantimonates are not known in the literature.

The first X-ray studies on diaquahydronium salts were reported by Olovsson[20] and later studies were reported by Follner,[21] Penneman and Ryan,[22] Brown et al.,[23] and Matheson and Whitla.[24] In these structures, the hydrogen atoms were not determined from difference Fourier syntheses. Further X-ray investigations in this field were carried out by Mootz et al.,[25−30] and other research groups,[31−33] who found the $H_5O_2^+$ cation to be present in crystalline hydrates of some acids. In these structures (refs 25−33), the hydrogen atoms were determined from difference Fourier syntheses.

Crystal Structure of $H_5O_2^+SbF_6^-$. The crystal data are summarized in Table 1. The $H_5O_2^+SbF_6^-$ crystallizes in the

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Table 2. Bond Lengths (Å), Selected Angles (deg), and Interionic Distances (Å) for $H_5O_2^+SbF_6^-$ [a]

Sb(1)−F(1)	1.855(5)	F(1)−Sb(1)−F(6)	178.8(2)
Sb(1)−F(2)	1.881(4)	F(2)−Sb(1)−F(5)	178.8(2)
Sb(1)−F(3)	1.875(5)	F(3)−Sb(1)−F(4)	176.7(2)
Sb(1)−F(4)	1.869(6)	F(1)−Sb(1)−F(2)	90.5(2)
Sb(1)−F(5)	1.865(5)	F(1)−Sb(1)−F(3)	92.2(2)
Sb(1)−F(6)	1.882(5)	F(2)−Sb(1)−F(4)	90.2(2)
O(1)···O(1a)	2.418(8)	O(2)···O(2b)	2.40(1)
O(1)−H(11)	1.130(6)	O(2)−H(21)	0.938(6)
O(1)−H(12)	0.961(6)	O(2)−H(22)	0.967(6)
O(1)−H(13)	1.209(6)	O(2)−H(23)	1.200(6)
O(1)···F(2c)	2.79(1)	O(2)···F(4e)	2.724(8)
O(1)···F(3d)	2.732(9)	O(2)···F(6c)	2.66(1)

[a] Symmetry transformations: (a) $-x$, $-y$, $1 - z$; (b) $1 - x$, $-y$, $-z$; (c) x, $y - 1$, z; (d) $-x$, $-y$, $-z$; (e) $1 - x$, $1 - y$, $1 - z$.

triclinic space group $P\bar{1}$ with two formula units per unit cell. For the data reduction, a semiempirical correction determined from ψ-scan data and structure solution and refinement programs in the SHELXTL package and PARST were used.[34,35] The antimony layers were found by the Patterson method. All atoms including protons were found in the difference Fourier synthesis, and a final refinement with anisotropic (except for H atoms) thermal parameters gave a value of $R = 0.038$. The relatively large value R(int) of 0.10 is probably caused by the crystal quality, since the crystals undergo dehydration on the surface during removal of HF.[36]

Bond lengths and selected angles are summarized in Table 2. The lengths of the Sb−F bonds and the F−Sb−F angles show only small deviations from an ideal octahedral geometry and are in good agreement with known octahedral hexafluoroantimonate anions.[37−39] The crystal packing contains two independent $H_5O_2^+$ ions. Both ions have an inversion center and almost identical O···O distances (2.417(8) and 2.40(1) Å) comparable to those of known $H_5O_2^+$ salts.[20−30] The H_2O ends of the $H_5O_2^+$ ions share one proton located in the inversion center of the ion which is approximately of symmetry C_{2h}.

All terminal H atoms of the cations have contacts to fluorine atoms of neighboring anions and are located along the O···F axes, which have distances in the range between 2.66(1) and 2.79(1) Å. The linkage of the anions and cations via the secondary H···F interactions (see Figure 1) results in a three-dimensional network in the crystal.

Synthesis of $Me_4N^+HPF_5^-$. The first synthesis of a hydridopentafluorophosphate was described by Nixon and Swain in 1969.[40,41] They obtained $KHPF_5$ by a reaction of KHF_2 with PF_3 in acetonitrile (eq 5).

$$PF_3 + KHF_2 \rightarrow KHPF_5 \qquad (5)$$

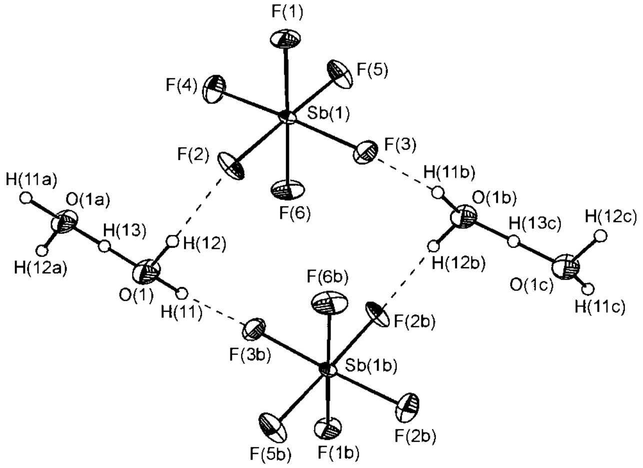

Figure 1. Projection of the two $H_5O_2^+$ species and their secondary contacts to neighboring SbF_6^- ions in $H_5O_2^+SbF_6^-$. Thermal ellipsoids are drawn at the 50% probability level. Symmetry transformations: (a) $-x$, $2 - y$, $1 + z$; (b) $-x$, $1 - y$, $-z$; (c) x, $y - 1$, $z - 1$.

Later, HPF_5^- salts were observed during treatment of trimethylamine with HPF_4, or reaction of the triethlyamine−HF adduct with phosphine derivates, respectively.[42−45] The formation of the HPF_5^- salts proceeds probably via an intermediate formation of HF_2^- salts and PF_3. More recently, Christe et al. described the formation of $Me_4N^+HPF_5^-$ by pyrolysis and hydrolysis of $Me_4N^+PF_4^-$ and reported a synthesis analogous to eq 5.[11,46,47] The HPF_5^- anion was characterized by NMR and vibrational spectroscopy, and structural parameters have been predicted by ab initio calculations,[11,40−46] but experimental data for bond lengths and angles are still unknown.

The $Me_4N^+HPF_5^-$ can alternatively be prepared by the reaction of HPF_4 with Me_4NF (eq 6) used already by us for the preparation of $CsHPF_5$.[48] The Me_4NF reacts with HPF_4 at −40 °C within 2 h with formation of the hydridopentafluorophosphate, which was identified by NMR and vibrational spectroscopy.

$$Me_4N^+F^- + HPF_4 \rightarrow Me_4N^+HPF_5^- \qquad (6)$$

The microcrystalline (size less than 5 μm) colorless solid obtained by this reaction is only slightly soluble in acetonitrile. Growing of single crystals suitable for X-ray diffraction studies was achieved by ultrasonic treatment of $Me_4N^+HPF_5^-$ suspended in acetonitrile.

Crystal Structure of $Me_4N^+HPF_5^-$. The characterization of $Me_4N^+HPF_5^-$ by NMR- and vibrational spectroscopy is well discussed by Christe and co-workers.[11,41] Therefore we describe here only the crystal structure of this salt. The single crystal investigated by X-ray diffraction studies was checked by Raman spectroscopy to confirm that its composition was identical to that of the bulk sample.

The crystal data are summarized in Table 1 (see also Figure 2). The $Me_4N^+HPF_5^-$ crystallizes in the tetragonal space group *P*4/*nmm* with two formula units per unit cell. For the data

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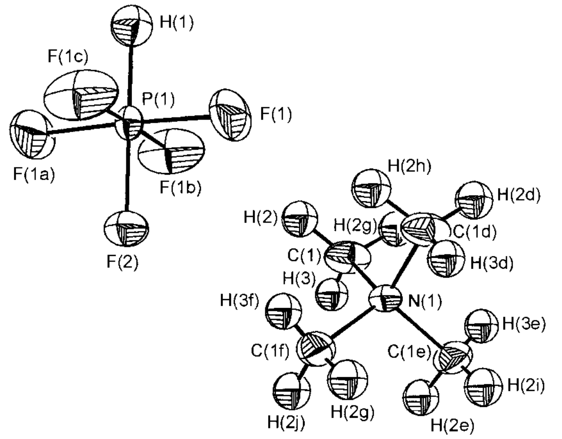

Figure 2. Asymmetric part of the unit cell of $Me_4N^+HPF_5^-$. Thermal ellipsoids are drawn at the 50% probability level. Summetry transformations: (a) $0.5 - y, x, z$; (b) $-x, 0.5 + y, -z$; (c) $0.5 + y, 0.5 + x, -z$; (d) $1.5 - y, x, z$; (e) $1.5 + x, 1 - y, 1 - z$; (f) $1 - y, -x, 1 - z$; (g) $2 - y, 0.5 + x, -z$; (h) $0.5 + x, 1.5 + y, -z$; (i) $x, -0.5 - y, 1 + z$; (j) $1.5 - y, 1.5 - x, 1 + z$.

Table 3. Bond Lengths (Å) and Selected Angles (deg) for $(CH_3)_4N^+HPF_5^-$ [a]

P(1)−F(1)	1.595(6)	C(1)−N(1)	1.486(8)
P(1)−F(2)	1.594(9)	C(1)−H(2)	1.07(6)
P(1)−H(1)	1.5(2)	C(1)−H(3)	0.82(9)
F(1)−P(1)−F(1a)	89.98(1)	C(1)−N(1)−C(1d)	109.7(3)
F(1) −P(1)−F(1b)	177.7(5)	C(1)−N(1)−C(1e)	109.0(7)
F(1)−P(1)−F(1c)	89.98(1)	C(1)−N(1)−C(1f)	109.7(3)
F(1)−P(1)−F(2)	88.8(2)	C(1d)−N(1)−C(1e)	109.7(3)
F(1)−P(1)−H(1)	91.2(2)	C(1d)−N(1)−C(1f)	109.0(7)
F(2)−P(1)−H(1)	180.00(2)	C(1e)−N(1)−C(1f)	109.7(3)

[a] Symmetry transformations: (a) $0.5 - y, x, z$; (b) $0.5 - x, 0.5 - y, z$; (c) $y, 0.5 - x, z$; (d) $y + 0.5, 1 - x, 1 - z$; (e) $1.5 - x, 0.5 - y, z$; (f) $1 - y, x - 0.5, 1 - z$.

reduction, a semiempirical correction determined from ψ-scan data and structure solution and refinement programs in the SHELXTL package and PARST were used.[34,35] The tetramethylammonium skeleton NC_4 and the PF_5 fragment of the anion were found by direct methods. The H atoms were found in the difference Fourier synthesis after anisotropic refinement of the heavier atoms. The final refinement was carried out without any constrained C−H and P−H bonds.[36]

The bond lengths and angles of the anion and cation are summarized in Table 3. The CN_4 skeleton of the cation has an almost ideal tetrahedral symmetry with C−N bond lengths (1.486(8) Å) which are normal for the Me_4N^+ ion.[49,50] The anion has a slightly distorted ψ-octahedral symmetry with four equal F atoms arranged in the equatorial position ($d(P-F_{eq}) = 1.595(6)$ Å) and one axial $P-F_{ax}$ bond with 1.594(9) Å. The electron density map indicates a P−H bond strictly in the axial direction. The P−H distance of 1.5(2) Å is of rather poor accuracy. However, because it is difficult to determine hydrogen atoms, we repeated the X-ray measurements on two other crystals, but the results were quite the same. Refinements of the structures with a fixed distance of 1.4 Å for P−H, which is common for P−H bonds,[38,11] showed no significant influence on the P−F distances. Thus, we are confident in determining correct geometrical parameters for the PF_5 skeleton. The crystal packing contains no interionic distances shorter than the van der Waals radii.

***Cis*- and *Trans*-Effect.** Mutual ligand interaction effects in monosubstituted ψ-octahedral complexes have been the subject of several studies.[51−53] Shustorovich and Buslaev proposed a qualitative model to predict such effects, and they introduced the terms *trans*- and *cis*-effect.[54] The *cis*-effect dominates in the case of a central atom in its highest oxidation state (formally preserving no ns^2 lone pair) if the substituting ligand causes a strengthening of the axial bond at the expense of a weakening of the equatorial bonds. The term *trans*-effect is used for the opposite case. Following the general considerations of Shustorovich and Buslaev the effect should be large for molecules with large differences in the donor ability of the ligands. Such a case is given in the HPF_5^- ion. Applying the qualitative model of Shustorovich and Buslaev, the hydrogen ligand should cause a *cis*-effect. This was supported by Christe et al., who predicted $r(P-F_{ax}) = 1.628$ Å and $r(P-F_{eq}) = 1.649$ Å on the basis of ab initio calculations.[11] However, the X-ray diffraction studies show no significantly different P−F distances, and the prediction can be neither confirmed nor rejected, since the effect is too small to be determined beyond doubt. Furthermore, the effect can be overlaid by the *site*-effect in the crystal which is imposed on the HPF_5^- anion by the crystal field, which is clearly evident from the band splitting of the P−H stretching vibration.

Another effect, which is confirmed by the X-ray study, is the slight but significant compression of the $F_{ax}-P-F_{eq}$ bond angle, which indicates that the effective repulsion from the hydrogen is somewhat larger than that from the fluorine ligand.[11]

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Supporting Information Available: Listings of crystal data and intensity collection parameters, anisotropic thermal parameters, and all bond lengths and angles (9 pages). Ordering information is given on any current masthead page.

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