Superacid Systems

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The Existence of Hexafluoroarsenic(V) Acid

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 70th birthday

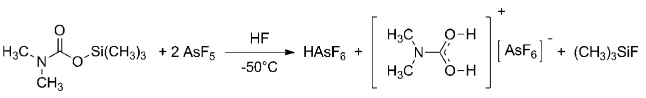
Abstract: *The homogeneous mixture of anhydrous hydrogen fluoride aHF and antimony pentafluoride AsF_5 is known as a superacidic system. The high acidity is derived from the formation of $[H_2F]^+$ $[AsF_6]^-$. No experimental evidence exists for the existence of the free acid molecule $HAsF_6$. The reaction of trimethylsilyl N,N-dimethylcarbamate in the binary system aHF/AsF_5 led to decomposition of trimethylsilyl N,N-dimethylcarbamate at −50 °C to dimethylammonium hexafluoridoarsenate and cocrystallization of $HAsF_6$. The single-crystal X-ray structure displays an $HAsF_6$ molecule involved in an asymmetric hydrogen bridge to the hexafluoridoarsenate anion. As a result of the incalculable situation in the crystal lattice, the molecular structure of $HAsF_6$ is calculated by quantum chemical structure optimization of the extreme cases of $[FHF\text{-}AsF_5]^-$ (strong hydrogen bond) and $HAsF_6$ (no hydrogen bond) at the PBE1PBE/6-311G(3df,3pd) level of theory.*

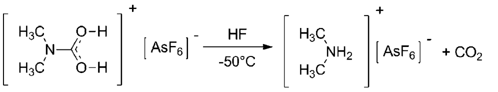
Acids which are more acidic than 100 % sulfuric acid are by definition "superacids". The term "superacids" was first introduced in 1927 by Conant and Hall.[1,2] The addition of Lewis acids leads to an increased acidity of strong Brønsted acids such as H_2SO_4, HSO_3F, and HF. Especially high acidities (H_0 up to −27) are achieved, for example, in the binary systems FSO_3H/SbF_5 (Magic Acid) and HF/SbF_5 (fluoroantimonic acid).[3,4] A less intense effect is shown by the pentafluorides of the lighter homologues PF_5 and AsF_5.[3,4] The superacid system HF/AsF_5 has until now been less investigated.

The superacid systems HF/MF_5 (M = As, Sb) can be described by the formation of $[H_2F]^+$ and $[MF_6]^-$ or higher oligomeric anions such as $[M_nF_{5n+1}]^-$.[5] In the case of HF/SbF_5, single crystals of the fluoronium salts $[H_2F]^+[Sb_2F_{11}]^-$ and $[H_3F_2]^+[Sb_2F_{11}]^-$ were characterized by X-ray structure analysis.[6] In aqueous solutions these compounds protonate water with formation of the oxonium salts $[H_3O]^+$ $[SbF_6]^-$ or $[H_3O]^+$ $[AsF_6]^-$, respectively. In the past it was believed that aqueous solutions contain dissolved hexafluoroantimonic acid ($HSbF_6$), hexafluoroarsenic acid ($HAsF_6$),[7] or tetrafluoroboric acid (HBF_4).[8] However, the water-free acids $HSbF_6$, $HAsF_6$, and HBF_4 are still unknown.

Even though the molecular species $HAsF_6$ has never been observed in solution, we surprisingly detected it in the solid state. The reaction of trimethylsilyl *N*,*N*-dimethylcarbamate with the superacid system HF/AsF_5 did not lead to the expected product, the protonated species of *N*,*N*-dimethylcarbamic acid. The reaction can be described by Equations (1)–(3). In the first step, the superacid HF/AsF_5 is formed at 0 °C to ensure a homogeneous mixture of the components *a*HF and AsF_5. In the next step, trimethylsilyl *N*,*N*-dimethylcarbamate reacts with HF and the superacid, probably with formation of the protonated species, which is decarboxylated in the next step. The reaction in Equation (2) shows elimination of trimethylsilyl fluoride under formation of protonated *N*,*N*-dimethylcarbamic acid. An immediate decomposition then leads to a *N*,*N*-dimethylammonium cation by elimination of carbon dioxide.

$$HF + HAsF_6 \xrightarrow[0^\circ C]{} [AsF_6]^- + [H_2F]^+ \qquad (1)$$


(2)


(3)

The evolution of gaseous carbon dioxide can be observed at −50 °C. Usually an excess of AsF_5 is completely removed in a dynamic vacuum. Only in a few cases are $As_2F_{11}^-$ ions formed instead of AsF_6^- ions.[9–11] It is crucial to maintain the temperature during the removal of the volatile reaction products between −50 °C and −55 °C. The solubility of the compounds is too low if the temperature is below −55 °C. Only the dimethylammonium hexafluoridoarsenate $[(CH_3)_2NH_2]^+[AsF_6]^-$ is observed if the temperature is above −50 °C.

The crystal structure of $[(CH_3)_2NH_2][AsF_6]\cdot HAsF_6$ (**1**) consists of the dimethylammonium cation $[(CH_3)_2NH_2]^+$, the AsF_6^- anion, and a $HAsF_6$ molecule.[12] The bond lengths and angles of the dimethylammonium cation are in the same range as described in the literature.[13] The AsF_6^- ion forms a slightly distorted octahedron, and the bond lengths and angles of the anion are in the normal range expected for AsF_6^-.[14] In $HAsF_6$, the fluorine atoms are arranged in a slightly distorted octahedron around the arsenic atom. The

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As1−F2, −F3, −F4, −F5, and −F6 bond lengths are in the range of normal As−F bonds (1.668–1.675 Å)[12] of AsF_6^- ions,[14] only the As1−F1 (1.979(2) Å) bond length is about 0.3 Å longer. Therefore, the four fluorine atoms in the equatorial plane are puckered in the direction of the fluorine atom F1, to which the hydrogen atom H1 is bound. A very strong hydrogen bridge (F1-H1···F12 (F···F distance: 2.309(3) Å)) exists between the hydrogen atom H1 of the $HAsF_6$ molecule and the AsF_6^- ion. This distance is about 0.05 Å longer than in the HF_2^- ion (F···F: 2.26 Å).[15] As a consequence of this hydrogen–fluorine bridge, one might assume at first sight that an $[AsF_6\cdots H\cdots AsF_6]^-$ ion exists. However, the long As1−F1 bond instead indicates that the hydrogen atom (H1) is located at this fluorine atom (F1). Therefore, the structure of $HAsF_6$ could also be described as a strong donor–acceptor adduct between HF and AsF_5. Two further hydrogen bridges between the $HAsF_6$ and the $[(CH_3)_2NH_2]^+$ ion form chains along the *c* axis involving the hydrogen bonds N1-H2···F3 and N1-H3···F5 [N···F distance: 2.920(4) Å and 3.032(4) Å; description of the network by graphset analysis C2,2(6)],[16] which are indicated in Figure 1.

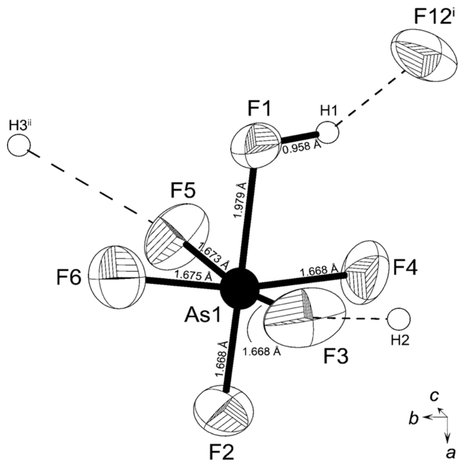

Figure 1. $HAsF_6$ molecule in the crystal showing intermolecular hydrogen bonds. Thermal ellipsoids are set at 50% probability. Symmetry codes: i = −*x*, −0.5 + *y*, 1.5−*z*; ii = *x*, 1.5−*y*, 0.5 + *z*.

A comparison of the $HAsF_6$ structure in the crystal lattice with calculated gas-phase structures is difficult, since the As1−F1 bond is strongly influenced by the hydrogen bridge. An asymmetric $[AsF_6\cdots H\cdots AsF_6]^-$ ion can not be calculated. Therefore, the two extreme cases of the AsF_5 complexes HF-AsF_5 and the negatively charged $[FHF\text{-}AsF_5]^-$ were calculated at the PBE1PBE/6-311G(3df,3pd) level.[17] The HF-AsF_5 complex, which represents a bare $HAsF_6$ molecule, has an As1−F1 bond length of 2.351 Å, which can be considered as an upper limit for an As−F bond. The $[FHF\text{-}AsF_5]^-$ ion has a calculated As1−F1 bond length of 1.776 Å, which represent the lower limit of an As−F bond in the case of a very strong hydrogen-bridged $HAsF_6$ molecule. The real situation in the crystal lattice is an As1−F1 bond with a length of 1.979(2) Å, which is between these extreme cases.

Experimental Section

First, arsenic pentafluoride (AsF_5, 340 mg, 2 mmol) and then an excess of anhydrous hydrogen fluoride (*a*HF; 3.00 g) were condensed into a reactor (FEP tube) by cooling at −196 °C. The reactor was allowed to warm up to 0 °C (ice bath) for about 10 minutes to mix the components and to form the superacid system. After cooling to −196 °C, trimethylsilyl *N*,*N*-dimethylcarbamate ($C_6H_{15}NO_2Si$; 161 mg, 0.17 mL, 1.0 mmol) was added under an inert atmosphere (nitrogen). The reaction mixture was allowed to warm to −50 °C for 10 minutes, and then cooled to −78 °C. The excess of hydrogen fluoride was removed under a dynamic vacuum at −78 °C, and colorless crystals were obtained. The crystals are stable under inert gas at a dry-ice temperature for several weeks and at −45 °C for only a few minutes.

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