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Editor's choice

The acid strength of the datively bound complexes involving AlF_3 lone pair acceptor and various lone pair donors

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ABSTRACT

The acid strength of the datively bound **X** → AlF_3 complexes (**X** = HF, HCl, H_2S, AsH_3, PH_3, NF_2H, NFH_2, NH_3, and H_2O) is evaluated on the basis of theoretical calculations employing ab initio methods. Significant enhancement of the **X** acidity upon the formation of **X**/AlF_3 compounds is predicted. It is demonstrated that even the non-acidic molecules **X** (e.g., H_2O, NH_3) combined with AlF_3 are expected to form the **X** → AlF_3 complexes characterized by the acid strength comparable or larger than that of H_2SO_4.

1. Introduction

The term "superacid" appeared in the literature for the very first time in the work of Hall and Conant published in 1927 [1]. A few decades later it was proposed to define superacids as the compounds whose acidity is stronger than that of 100% sulfuric acid which means that their Hammett acidity function (H_0) is smaller than −12 [2,3]. However, the superacid chemistry has only become a widespread area when Olah and Hogeveen published their reports on the stability of carbocations [4–9]. These studies triggered the continuing theoretical [10–15] and experimental [16–23] investigations concerning various superacids' properties, such as structures, stabilities and acid strengths. Our group contributed to these studies by (i) providing the evaluation of the acid strength of a series of aluminum-based Lewis–Brønsted superacids (HF/AlF_3 ($HAlF_4$), HF/Al_2F_6 (HAl_2F_7), HF/Al_3F_9 (HAl_3F_{10}), and HF/Al_4F_{12} (HAl_4F_{13}))[24] and the similar superacids containing In, Sn, and Sb (HIn_nF_{3n+1}, HSn_nF_{4n+1}, and HSb_nF_{5n+1} (n = 1–3)) [25], as well as Ti and Ge (HTi_nF_{4n+1} and HGe_nF_{4n+1} (n = 1–3)) [26]; (ii) determining that the protonation of superhalogen anions [27–29] might be considered as the route to superacids' formation in selected cases [30,31]; (iii) emphasizing the importance of microsolvation effects on the acidity of the systems containing the excess of either Brønsted acid component (i.e., nHF/AlF_3 and nHF/GeF_4 (n = 1–6)) [32] or Lewis acid component ($HClO_4$/n(AlF_3) and $HClO_4$/n(SbF_5) (n = 1–3)) [33]; and (iv) demonstrating that certain hydrogenation reactions (e.g., carbon monoxide hydrogenation yielding formaldehyde) might be catalyzed by either $HAlF_4$ or $HSbF_6$ superacid [34,35].

The binary Lewis–Brønsted superacids are commonly prepared by mixing Brønsted acid (B) and strong Lewis acid (L), hence the structure of the representative building block consists of a pair of B and L molecules held together by mutual interactions. The most important feature of such a building block is the presence of a B → L dative bond. For example, the structure of $HAlF_4$ should be written as HF → AlF_3 which illustrates that the fluorine electron lone pair of the HF Brønsted acid molecule is being donated to the empty 3p aluminum orbital of the Lewis acid molecule. Moreover, the whole HF → AlF_3 system is additionally stabilized by the hydrogen bond [36]. The presence of the dative bond in the Lewis–Brønsted superacids is crucial as it strongly affects the resulting distribution of the electron density in the system, namely, the electron density is moved toward the Lewis acid component (e.g., AlF_3) which usually increases the polarity of the B → L complex. As a consequence, the Brønsted acid component (e.g., HF) exhibits electron density deficit which in turn weakens the H—F bond and thus increases the acid strength.

Earlier studies on many Lewis–Brønsted superacids revealed that their acidity (manifested by the Gibbs free energies of the superacid deprotonation reactions (ΔG^{298}_{acid})) may vary to span approximately 230–303 kcal/mol range (where ΔG^{298}_{acid} of 303 kcal/mol is the limiting value for superacids as it corresponds to the Gibbs free deprotonation energy of the sulfuric acid as measured by Viggiano et al. [37] and confirmed by theoretical calculations [11]). In particular, the strongest Lewis–Brønsted superacid

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proposed thus far (HSb_3F_{16}) is characterized by ΔG^{298}_{acid} = 230 kcal/mol [25] while the values predicted for other systems are somewhat larger (e.g., 240 kcal/mol for HAu_3F_{16} [31], 265 kcal/mol for $HGaCl_4$ [30], 272 kcal/mol for $HBeCl_3$ [13], 281 kcal/mol for HPF_6 [13]). Clearly, the acid strength of the Lewis–Brønsted superacid strongly depends on the choice of both L and B components that a given acid consists of. Despite a large number of superacids investigated thus far, this issue has not been systematically addresses yet. Therefore, in this contribution, we describe our studies on the **X**/AlF_3 (**X** → AlF_3) compounds, where **X** is the neutral closed-shell molecule capable of acting as electron lone pair donor. In order to provide the results covering the cases where the efficiency of the predicted electron density flow (from **X** to AlF_3) varies, we chose the set of commonly known molecules to act as lone pair donors whose acidity is either apparent (e.g., HF, HCl, H_2S) or almost negligible (e.g., H_2O, NH_3). We hope that the results we provide will help the experimental chemists in designing novel Lewis-Brønsted superacids exhibiting the desired acid strength.

2. Methods

The **X**/AlF_3 (**X** = HF, HCl, H_2S, AsH_3, PH_3, NF_2H, NFH_2, NH_3, and H_2O) closed-shell neutral systems (i.e., complexes consisting of the AlF_3 Lewis acid forming dative bond with **X** molecule) and their corresponding anions (i.e., negatively charged closed-shell species formed by deprotonation thereof) were investigated using theoretical quantum chemistry methods. In particular, the equilibrium geometries and harmonic vibrational frequencies were calculated using the quadratic configuration interaction method with single and double excitations (QCISD) [38–40] with the aug-cc-pVDZ basis set [41] (for H, F, Cl, N, P, As, O, and S) and the aug-cc-pV(D + d)Z basis set [42] (for Al).

The Gibbs free energies of the deprotonation reactions (ΔG^{298}_{acid}) concerning the isolated **X** molecules (HF, HCl, H_2S, AsH_3, PH_3, NF_2H, NFH_2, NH_3, and H_2O) and their complexes with AlF_3 were evaluated using the electronic energies, zero-point energy corrections, thermal corrections and entropy contributions (at T = 298.15 K) estimated with the QCISD method and the same basis sets. In each case the Gibbs free energy of the proton was also accounted for.

The gas-phase basicity (also called absolute or intrinsic basicity) of each **X** molecule (ΔG^{298}_{base}) was calculated as the negative of the Gibbs free energy change associated with the $\boldsymbol{X} + H^+ \rightarrow \boldsymbol{X}H^+$ reaction (with the Gibbs free energy of the proton accounted for). Such defined ΔG^{298}_{base} values were evaluated using the electronic energies, zero-point energy corrections, thermal corrections and entropy contributions (at T = 298.15 K) estimated with the QCISD method and the same aug-cc-pVDZ/aug-cc-pV(D + d)Z basis sets.

In order to verify the reliability of the QCISD/aug-cc-pVDZ theory level applied, we refined our calculations (including geometry optimizations and harmonic vibrational frequency calculations) for two **X**/AlF_3 complexes (we chose the most weakly bound and the most strongly bound systems, namely HCl/AlF_3 and NH_3/AlF_3 whose binding energies are equal to 10.5 and 40.7 kcal/mol, respectively) at the more advanced CCSD(T)/aug-cc-pVTZ level. We found that the Gibbs free deprotonation energies evaluated for these two complexes by using the CCSD(T) method and the aug-cc-pVTZ basis set differ from those predicted by employing the QCISD method and the aug-cc-pVDZ basis set by less than 1 kcal/mol. Therefore, we are confident that the theory level applied in this contribution (i.e., QCISD/aug-cc-pVDZ/aug-cc-pV(D + d)Z) is adequate and reliable.

The partial atomic charges were evaluated by the Natural Bond Orbital (NBO) analysis scheme [43–45] using the QCISD electron densities.

All calculations were performed using the GAUSSIAN16 (Rev. B.01) package [46].

3. Results

The equilibrium structures of the HF/AlF_3, HCl/AlF_3, H_2S/AlF_3, AsH_3/AlF_3, PH_3/AlF_3, NF_2H/AlF_3, NFH_2/AlF_3, NH_3/AlF_3, and H_2O/AlF_3 systems and their corresponding deprotonation products are presented and described in this section whereas the Cartesian coordinates of all systems studied are provided in the Supporting Information (see Table S1). All systems analyzed correspond to energetic minima (as confirmed by frequency analysis).

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2018.06.059.

3.1. Equilibrium structures of the X/AlF_3 systems and their deprotonated forms

While designing our **X**/AlF_3 systems we have chosen the set of structurally simple closed-shell molecules **X** which contain both (i) at least one hydrogen atom (needed to assure that the resulting **X**/AlF_3 compound may act as a system capable of donating a proton) and (ii) electron lone pair that could be donated to the empty 3*p* Al orbital of AlF_3 (see the hybrid compositions presented in Table S2 in the Supporting Information). In addition, while choosing the **X** molecules we wanted to include the systems whose acidity/basicity varies. Therefore, each of the systems we have chosen is capable of acting as a proton donor (i.e., Brønsted acid) and as an electron lone pair donor (i.e., Lewis base).

The equilibrium structures of the NH_3/AlF_3, $(NH_2/AlF_3)^-$, H_2O/AlF_3, $(HO/AlF_3)^-$, NFH_2/AlF_3, and $(NFH/AlF_3)^-$ are presented in Fig. 1, the structures of PH_3/AlF_3, $(PH_2/AlF_3)^-$, NF_2H/AlF_3, $(NF_2/AlF_3)^-$, AsH_3/AlF_3, and $(AsH_2/AlF_3)^-$ are shown in Fig. 2, whereas those of the H_2S/AlF_3, $(HS/AlF_3)^-$, HCl/AlF_3, $(Cl/AlF_3)^-$, HF/AlF_3, and $(F/AlF_3)^-$ are depicted in Fig. 3 (all structures presented correspond to energetic minima, as confirmed by frequency analysis).

In general, the structures of the neutral **X**/AlF_3 systems contain the non-planar AlF_3 fragment and the **X** molecule tethered to it via the dative bond (see the dashed lines in Figs. 1–3). In most cases considered, the hydrogen atoms of the **X** systems form the H-bonds with the fluorine ligands connected to the Al atom (see the dotted lines in Figs. 1–3) which provides the additional stabilization. As a consequence, the binding energies (BE) predicted for the **X**/AlF_3 complexes are positive and span the 10.5–40.7 kcal/mol range, see Table 1 (binding energy for each **X**/AlF_3 complex was calculated by subtracting the energies of the isolated and relaxed (i.e., separately optimized) **X** and AlF_3 species from that of the **X**/AlF_3 compound). The positive values of the Gibbs free fragmentation energies (with respect to the **X**/AlF_3 → **X** + AlF_3 process) also support the stability of all systems considered, see Table 1.

As expected, the length of the **X** → Al dative bond strongly depends on the choice of the **X** component, namely, the shortest separation (1.968 Å) was found for H_2O/AlF_3 whereas the longest dative bond length (2.613 Å) was predicted for AsH_3/AlF_3. In all neutral cases the AlF_3 fragment adopts pyramidal structure (i.e., it is deformed from its planar D_{3h}–symmetry structure exhibited by the isolated aluminum trifluoride) with the Al—F bond lengths spanning the relatively narrow 1.653–1.674 Å range. The lengths of the hydrogen bonds in the **X**/AlF_3 systems are related to both (i) the separations between **X** and AlF_3 fragments (which in turn is caused by the differences in atomic radii of N, P, As, O, S, Cl, and F atoms) and (ii) the mutual orientation of the **X** and AlF_3 subunits. The shortest H–bonds (i.e., 2.237 Å in HF/AlF_3, 2.564 Å in HCl/AlF_3, 2.603 Å in H_2O/AlF_3, 2.779 Å in NH_3/AlF_3) are predicted