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Does the protonation of superhalogen anions always lead to superacids?

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A R T I C L E I N F O

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The results of a thorough theoretical search for novel superacids are presented. The thermodynamic stability and the expected acidity strength of Lewis/Brønsted superacids (considered here as consisting of superhalogen anions and the additional protons) are examined for the systems containing selected alkali metals, alkali earth metals, metalloids and non-metals. The acidities of such designed systems involving alkali earth metals (Be, Mg, Ca) and 13th group elements (B, Al, Ga) evaluated by the estimation of Gibbs free energies of deprotonation reactions were found significant whereas the analogous species utilizing remaining elements as central atoms are not expected to exhibit superacidic properties.

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1. Introduction

The ‘superacid concept’ introduced by Hall and Conant in 1927 [1] was an important extension of the understanding of acidity (viewed as molecule’s ability to donate a proton in chemical reactions [2]). The superacid chemistry, however, was developed mainly by Olah and Hogeveen [3–8] and by Gillespie [9,10] who defined ‘superacid’ as any system exhibiting stronger acidity than 100% H_2SO_4 or with a Hammett acidity function smaller than -12. Since then, a large body of work was established concerning this subject [11–13], including relatively recent studies [14–19]. Our group contributed by investigating the $HAlCl_4$ stability issue [20], predicting the acidity of several aluminum-based HAl_nF_{3n+1} ($n = 1–4$) compounds [21], and describing dissociative excess electron attachment process with respect to the $HAlF_4$ superacid [22]. Despite the fact that certain systems might behave as strong acids in gas phase and relatively weak acids in liquid media [23], the gas phase acidity of a compound remains a very useful preliminary criterion allowing to search for novel possibly strong superacids. Having this reservation in mind, we utilize the Gibbs free energy of the deprotonation process to predict the gas phase acidity of a given system.

Since the superacids are very often prepared as the mixtures of strong Lewis acids and strong Brønsted acids, in the course of our previous studies we focused on the observation that many such obtained systems might be viewed as composed of a so-called superhalogen anion [24–26] (e.g., SbF_6^-, AlF_4^-, AsF_6^-) and a proton. Indeed, the well-known superhalogen anions are in fact the products of the superacid deprotonation processes. Thus the acidity of the superacid should likely be related to the electronic stability of the corresponding anion whose formation is a consequence of the superacid’s deprotonation. We preliminary explored this idea by investigating the series of aluminum-based superacids [21], i.e., $HAlF_4$, HAl_2F_7, HAl_3F_{10}, and HAl_4F_{13}. Namely, the estimated Gibbs free deprotonation energies of the HAl_nF_{3n+1} ($n = 1–3$) superacids were found significant and comparable to the corresponding value characterizing the $HTaF_6$, whereas the strength of the HAl_4F_{13} acid was predicted to exceed that of the $HSbF_6$ acid (the strongest liquid superacid recognized thus far) [21].

In this contribution we present the results of our more thorough search for novel promising superacids. Taking into account that the most stable superhalogen anions are those utilizing fluorine and chlorine ligands [27], we decided to take a closer look at the corresponding superacid compounds based on such negatively charged systems and involving various alkali metals, alkali earth metals, metalloids, and non-metals as central atoms.

2. Methods

The $HLiX_2$, $HNaX_2$, HKX_2, $HBeX_3$, $HMgX_3$, $HCaX_3$, HBX_4, $HAlX_4$, $HGaX_4$, HCX_5, $HSiX_5$, and $HGeX_5$ ($X = F, Cl$) systems and their corresponding anions (i.e., negatively charged systems formed by deprotonation) were investigated using theoretical quantum chemistry methods. In particular, the equilibrium geometries and harmonic vibrational frequencies were calculated using second-order Møller–Plesset perturbational method (MP2) and the 6-311++G(d,p) [28,29] basis sets. The final electronic energies of all such determined structures were obtained by applying the quadratic configuration interaction method with single and double substitutions (QCISD) [30–32] with the enlarged 6-311++G (2df,2pd) basis set.

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The Gibbs free energies of the deprotonation reactions (ΔG_{acid}) were evaluated using the QCISD/6-311++G(2df,2pd) electronic energies and the zero-point energy corrections, thermal corrections (at $T = 298.15$ K) and entropy contributions estimated with the MP2 method and 6-311++G(d,p) basis set (in each case the Gibbs free energy of the proton was also accounted for). The electronic and Gibbs free energies of the HX (X = F, Cl) molecule elimination (termed *EE* and ΔG_{elim}, respectively) were established accordingly, by using the described electronic and zero-point energies, thermal corrections and entropy contributions with respect to the $HMX_n \rightarrow MX_{n-1} + HX$ reaction (M = Li, Na, K ($n = 2$); Be, Mg, Ca ($n = 3$); B, Al, Ga ($n = 4$); C, Si, Ge ($n = 5$); X = F, Cl).

The BSSE (Basis Set Superposition Error) effects were neglected during our computations since we verified that their impact on the deprotonation energies of the species considered in this contribution is rather small (i.e., not exceeding 3 kcal/mol, which corresponds to 1–2% of the deprotonation energy values).

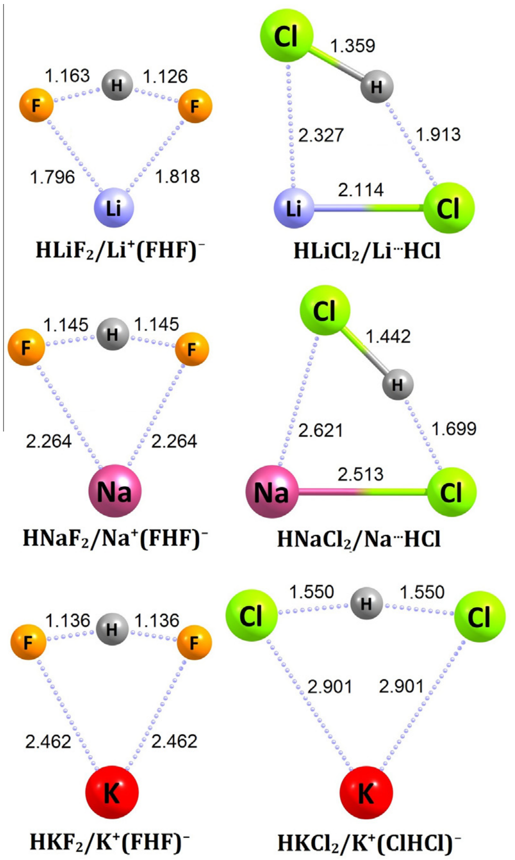
All calculations were performed with the GAUSSIAN09 (Rev. A.02) package [33].

3. Results

Since our main goal was to address the issue of possible superacid formation by the protonation of superhalogen anions, we performed our calculations for the HMX_{k+1}/MX_{k+1}^- pairs (each pair includes MX_{k+1}^- superhalogen anion and the corresponding HMX_{k+1} compound) containing representative alkali metal atoms (Li, Na, K), alkali earth metal atoms (Be, Mg, Ca), and the atoms belonging to the 13th (B, Al, Ga) and 14th (C, Si, Ge) groups playing the central atom role (M), whereas the F and Cl halogen atoms were utilized as ligands X. Hence, we believe that at least the most commonly investigated elements belonging to the main groups of the Mendeleev's Periodic Table were covered. We are aware of the fact that our arbitrary choice left a few important elements without consideration (such as P, S, and Sb), however, our hope is that concerning the proposed set of compounds allows to formulate fairly general conclusions.

In order to judge whether the investigated HMX_{k+1} system might be considered as a superacid we assumed the following criteria: (i) the acidity approximated by the Gibbs free deprotonation energy should not exceed 300 kcal/mol (since the analogous value for H_2SO_4 is 303 kcal/mol) [34], (ii) its structure must be intact and consisting of two clearly distinguishable MX_k and HF (or HCl) fragments (as it is the case for all Lewis/Brønsted superacids), and (iii) the HMX_{k+1} compound should be thermodynamically stable (although some exceptions are possible, as we explain in the following sections).

3.1. The $HLiX_2$, $HNaX_2$, and HKX_2 systems (X = F, Cl)



$HLiF_2/Li^+(FHF)^-$ $HLiCl_2/Li^{\cdots}HCl$

$HNaF_2/Na^+(FHF)^-$ $HNaCl_2/Na^{\cdots}HCl$

$HKF_2/K^+(FHF)^-$ $HKCl_2/K^+(ClHCl)^-$

Fig. 1. The MP2/6-311++G(d,p) equilibrium structures of the $HLiX_2$, $HNaX_2$, and HKX_2 systems (X = F, Cl). The bond lengths are given in Å.

Table 1
The deprotonation energies (*DE*), Gibbs free deprotonation energies (ΔG_{acid}), elimination energies (*EE*), and Gibbs free elimination energies (ΔG_{elim}) calculated at the QCISD/6-311++G(2df,2pd) (electronic energies) and MP2/6-311++G(d,p) (zero-point, thermal and entropy corrections at $T = 298.15$ K) level for MP2/6-311++G(d,p) equilibrium geometries. All energies in kcal/mol.

System	Symmetry	*DE*	ΔG_{acid}	*EE*	ΔG_{elim}
$HLiF_2$	C_s	333.6	323.0	24.4	16.6
$HLiCl_2$	C_s	294.2	285.1	12.1	4.2
$HNaF_2$	C_{2v}	348.2	337.0	28.1	19.1
$HNaCl_2$	C_s	301.5	292.8	13.1	5.9
HKF_2	C_{2v}	363.1	350.9	31.9	23.7
$HKCl_2$	C_{2v}	310.6	302.5	14.1	8.2
$HBeF_3$	C_s	299.7	288.4	10.3	1.9
$HBeCl_3$	C_s	282.9	273.2	4.5	−3.6
$HMgF_3$	C_s	306.5	294.8	18.9	10.3
$HMgCl_3$	C_s	280.3	270.8	10.0	2.35
$HCaF_3$	C_{2v}	320.2	309.9	25.2	16.0
$HCaCl_3$	C_s	283.2	274.0	11.5	2.9
HBF_4	C_s	301.5	292.7	3.8	−3.6
$HBCl_4$	C_s	297.2	292.0	1.6	−3.7
$HAlF_4$	C_s	279.8	269.2	16.4	7.1
$HAlCl_4$	C_s	271.4	263.4	8.3	0.2
$HGaF_4$	C_s	284.9	274.4	14.3	5.4
$HGaCl_4$	C_s	273.4	265.4	6.4	−1.4
HCF_5	C_s	375.9	366.6	1.1	−2.7
$HCCl_5$	C_s	338.5	328.5	2.0	−3.6
$HSiF_5$	C_s	308.5	300.0	2.5	−3.5
$HSiCl_5$	C_s	318.3	311.5	1.5	−3.8
$HGeF_5$	C_s	294.9	285.6	3.9	−3.0
$HGeCl_5$	C_s	310.1	303.9	1.7	−3.4

The equilibrium structures of $HLiF_2$, $HLiCl_2$, $HNaF_2$, $HNaCl_2$, HKF_2, and $HKCl_2$ are depicted in Fig. 1 while their deprotonation energies (*DE*), Gibbs free deprotonation energies (ΔG_{acid}), and the Gibbs free elimination energies (ΔG_{elim}, describing the susceptibility to either HF or HCl loss) are gathered in Table 1. Clearly, the $HLiF_2$ system consists of FHF^- and Li^+ which is confirmed by short F—H distances (ca. 1.1 Å) that are typical for an isolated FHF^- anion, relatively large Li—F separations (ca. 1.8 Å) indicating the absence of covalent Li—F bonds and the partial atomic charge of +0.84 a.u. predicted for the Li. Because the deprotonation Gibbs free energy of $HLiF_2$ (323.0 kcal/mol) is larger than our reference 300 kcal/mol value and related to the ΔG_{acid} of the isolated HF (370.9 kcal/mol, as calculated at the same theory level) we do not consider this system as superacid (instead, it represents the FHF^-Li^+ ionic compound). On the other hand, the equilibrium geometry of the $HLiCl_2$ corresponds to the desired LiCl/HCl structure (confirmed by the partial atomic charges on the HCl moiety that sum up to ~0 a.u.) connected via the LiCl·HCl hydrogen

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