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The Nature of Superacid Electrophilic Species in HF/SbF_5: A Density Functional Theory Study

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Abstract: A density functional theory study at the B3LYP/6-31++G** + RECP(Sb) level of the HF/SbF_5 superacid system was carried out. The geometries of possible electrophilic species, such as $H_2F^+{\cdot}Sb_2F_{11}^-$ and $H_3F_2^+{\cdot}Sb_2F_{11}^-$, were calculated and correspond with available experimental results. Calculations of different equilibrium reactions involving HF and SbF_5 allowed the relative concentration of the most energetically favorable species present in 1:1 HF/SbF_5 solutions to be estimated. These species are $H^+{\cdot}Sb_2F_{11}^-$, $H_2F^+{\cdot}Sb_2F_{11}^-$, $H_3F_2^+{\cdot}Sb_2F_{11}^-$, and $H_4F_3^+{\cdot}Sb_2F_{11}^-$, which correspond to 36.9, 16.8, 36.9, and 9.4%, respectively. Calculations of the acid strength of the electrophilic species were also performed and indicated that, for the same anion, the acid strength increases with the solvation degree. The entropic term also plays a significant role in proton-transfer reactions in superacid systems.

I. Introduction

The chemistry of liquid superacid media has been the subject of extensive research since the 1960s.[1] On one hand, liquid superacid media allow the limits of acidity in the condensed phase to be probed, and, on the other hand, they favor the formation and stabilization of energetic species, like carbocations, and activation of molecules of low reactivity, such as alkanes under mild conditions. Chemical reactions such as coal liquefaction, hydrocarbon isomerization, cracking, and alkylations are important industrial processes that occur under strongly acidic conditions. Brønsted superacids are defined as acids stronger than 100% H_2SO_4 ($H_o = -12$).[1] For Lewis acids, superacidity holds for any acid stronger than anhydrous $AlCl_3$.[1] A special category of superacids is generally obtained by the combination of a strong Brønsted acid with a strong Lewis acid, such as HSO_3F/SbF_5 and HF/SbF_5. The latter system is believed to possess the strongest acidity in the condensed phase, with $H_o = -23$,[2] depending on the relative molar ratio of the Brønsted and Lewis acids. It is believed that one of the reasons for the strong superacidity of this system is the formation of solvated H_2F^+ ions ($H_2F^+(HF)_n$) and $SbF_6^-(HF)_n$ or more associated species ($Sb_2F_{11}^-$, $Sb_3F_{15}^-$, etc.).

Spectroscopic studies, using ^{1}H and ^{19}F NMR[3] and IR,[4] of HF/SbF_5 with different molar ratios indicate that species such as H_2F^+, $H_3F_2^+$, and more solvated cations exist in equilibrium in these media, as well as SbF_6^- and $Sb_2F_{11}^-$. It was found that, for SbF_5 concentrations lower than 10 mol %, the SbF_6^- ion is practically the only anionic species present. From 10 to 22 mol % SbF_5 in HF, the anions are essentially SbF_6^- and $Sb_2F_{11}^-$, which are in a slow equilibrium, while more polymerized anions are found for higher SbF_5 concentrations.

$$2HF + SbF_5 = H_2F^+ + SbF_6^-$$

An interesting fact is that there is a small but increasing amount of un-ionized SbF_5 for concentrations above 25 mol %.[3a] This species could be involved in the direct oxidation of alkanes to carbenium ions plus hydrogen, when the concentration of SbF_5 in HF is higher than 25 mol %.[5]

Bonnet and Mascherpa[4] carried out IR studies of the HF/SbF_5 system and found that the solvated $H_3F_2^+$ is the predominant cationic species over a concentration range of 0−20 mol % of SbF_5. In the range of 20−40 mol % of SbF_5, only $H_3F_2^+$ was observed. The fluoronium ion, H_2F^+, is observed only in concentrated solutions, with more than 40 mol % SbF_5. At a HF/SbF_5 molar ratio of 2:1, the ionic species predominantly found are $H_3F_2^+(HF)_n$ and $Sb_2F_{11}^-$, instead of H_2F^+ and SbF_6^- ions. The cationic species (H_2F^+, $H_3F_2^+$, $H_{n+1}F_n$) are in rapid equilibrium on the NMR time scale, not allowing the observation of separate signals for each structure. Nevertheless, the ^{1}H NMR chemical shifts of these solutions vary from 8 (neat HF) to 16 ppm (80 mol % of SbF_5). The continuous variation in the chemical shifts is in good agreement with the degree of proton solvation, which is related to the concentration of HF molecules.

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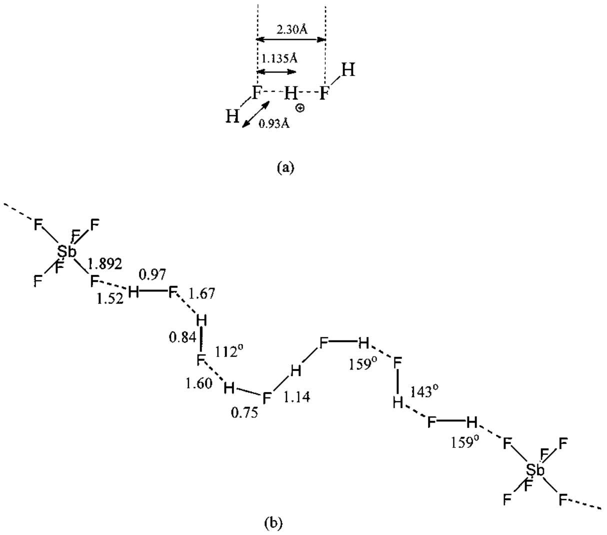
Scheme 1 [a]



[a] (a) $H_3F_2^+ \cdot Sb_2F_{11}^-$ X-ray structure in the 3:2 HF/SbF_5 adduct (33.3 mol % SbF_5)[6] and (b) the solvated $H_3F_2^+ \cdot (HF)_4$ in the HF/SbF_5 7:1 adduct (12.5 mol % SbF_5).[7]

Mootz and Bartmann were able to crystallize and elucidate the structure of HF/SbF_5 adducts, those with 1:1,[6] 3:2,[6] and 7:1 molar ratios.[7] They found that the crystals of the 1:1 adduct (50 mol % SbF_5) correspond to a complex of the H_2F^+ cation associated to the $Sb_2F_{11}^-$ anion. In the 3:2 adduct (33 mol % SbF_5), the species found was the $H_3F_2^+$ cation associated with the $Sb_2F_{11}^-$ anion (Scheme 1a), while in the 7:1 adduct (12.5 mol % SbF_5), a linear $H_3F_2^+$ species, solvated by four HF molecules, was found to exist sandwiched by two SbF_6^- anions (Scheme 1b).

Despite the numerous experimental available data for the HF/SbF_5 systems,[3,4,6,7] very few theoretical investigations using ab initio or density functional theory (DFT) methods were carried out for these systems.[8,9] This is probably associated with the difficulty of accurately dealing with the electronic structure of antimony atoms. Recently we performed DFT calculations on the alkane activation by some simple models of the HF/SbF_5 system aiming to get a better comprehension of the role of the anions and solvation of the carbocation.[8] Kim and Klein[9] carried out interesting ab initio molecular dynamics simulations on a highly diluted liquid HF/SbF_5 superacid with a molar ratio of 25:1 (3.8 mol % SbF_5). They found that the reaction of HF with SbF_5 is exothermic, barrierless, and diffusion-limited, yielding the SbF_6^- and the H_2F^+ cation, which is, in fact, a protonated HF chain. These chains are held together by hydrogen bonds, forming a zigzagged conformation. The system shows a fast proton jump, which explains the high molar conductance observed for diluted HF/SbF_5 solutions.[10] They also calculated the structure of a gas-phase complex of $SbF_5 + (HF)_{1-3}$. However, the calculation takes into account only one SbF_5 molecule, which of course is not well suited to represent correctly concentrated HF/SbF_5 solutions.

Thus, because of the lack of detailed investigation of these systems, at the molecular point of view, especially for higher SbF_5 contents, we started a theoretical study to elucidate the nature and stability of the active electrophilic species in the HF/SbF_5 solutions.

II. Computational Details

Calculations of the structure of finite models of the electrophilic species present in HF/SbF_5 solutions were carried out using the DFT approximation, at the B3LYP level of theory. The 6-31++G** basis set was used for all atoms, except the antimony atoms, where a relativistic effective core potential (RECP) was used to represent the core electrons.[11] This level of calculation will be represented as B3LYP/6-31++G** + RECP(Sb) from now on. Prior calculations[8b] showed that this level of theory provides good results. We used the Gaussian 98[12] package for performing these calculations.

The structures were characterized by the absence of imaginary frequencies. All the energies corresponding to the optimized structures were corrected for zero point energy (ZPE) and to 298.15 K and 1 atm. Unless otherwise stated, all energy discussion refers to the enthalpic term.

Because of the high complexity of the system, we focused on the 50 mol % solution of HF/SbF_5 (1:1 molar ratio). Nevertheless, it was possible to get insights into solutions with different molar ratios.

III. Results and Discussion

Figure 1 shows possible equilibrium reactions present in HF/SbF_5 solutions with the geometries computed at B3LYP/6-31++G** + RECP(Sb). Table 1 summarizes the thermodynamic properties for the equilibria shown in Figure 1.

HF/SbF_5 1:1. Table 2 contains the predicted values for ΔH, ΔS, and ΔG at 298.15 K and 1 atm for the reaction of four SbF_5 with four HF molecules (molar ratio HF/SbF_5 = 1:1) as a minimum ensemble model, producing several electrophilic species. The use of four molecules of each reactant was considered to guarantee a minimal set (molecularity) for the understanding of the chemical equilibria involving more condensed anions with a higher solvation degree.

If one considers the chemical equations

$$4SbF_5 + 4HF \rightleftharpoons 2H_2F^+ \cdot Sb_2F_{11}^- \qquad \Delta G = -19.4 \text{ kcal/mol}$$

$$4SbF_5 + 4HF \rightleftharpoons H_3F_2^+ \cdot Sb_2F_{11}^- + H^+ \cdot Sb_2F_{11}^- \qquad \Delta G = -20.4 \text{ kcal/mol}$$

$$4SbF_5 + 4HF \rightleftharpoons H_4F_3^+ \cdot Sb_2F_{11}^- + Sb_2F_{10} \qquad \Delta G = -18.8 \text{ kcal/mol}$$

as being the most important for the formation of the electrophilic

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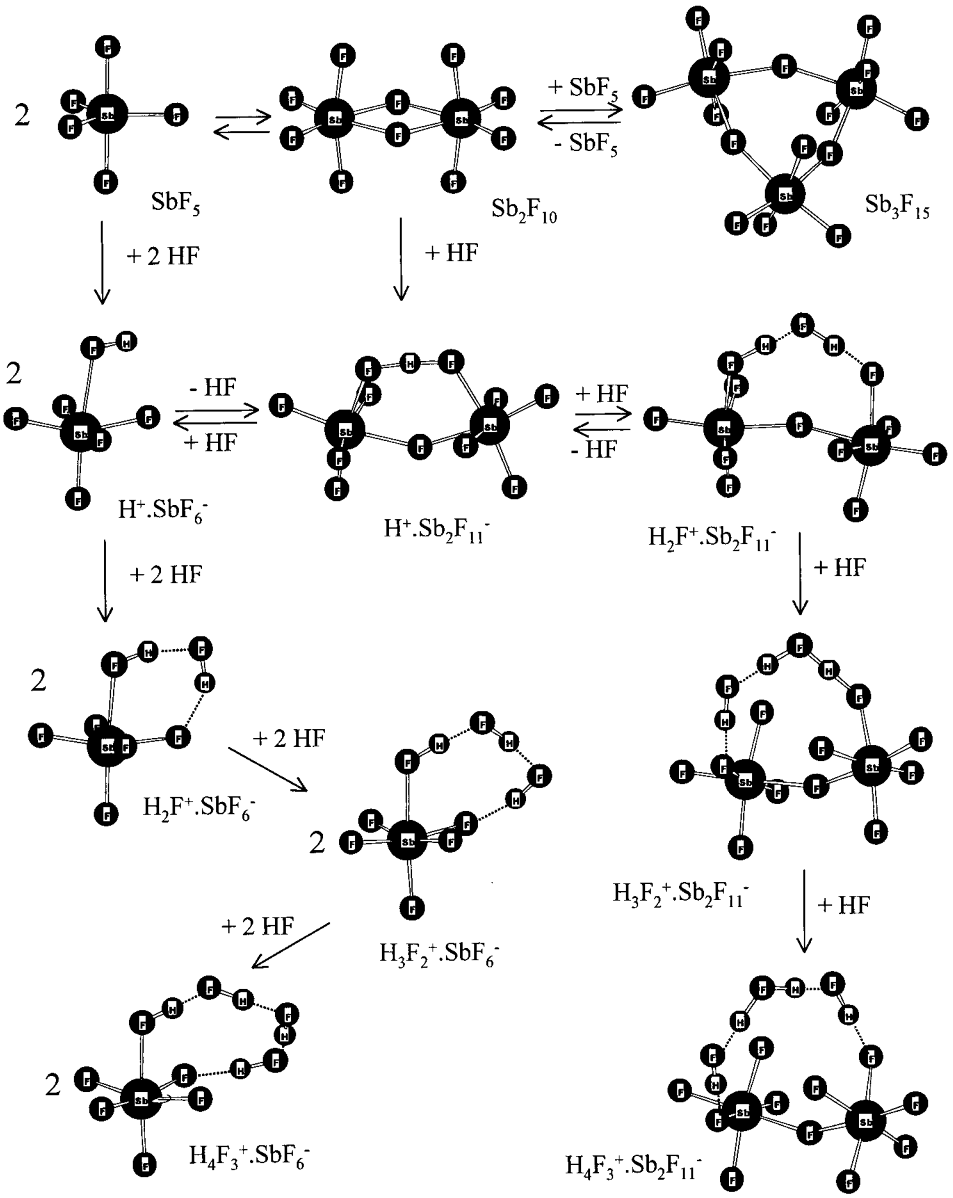

Figure 1. Predicted geometries for the different electrophilic species, associated to the SbF_6^- and $Sb_2F_{11}^-$ anions, formed by successive addition of HF molecules.

species (more negative ΔG), it is possible to write the following new equilibria

$$2H_2F^+{\cdot}Sb_2F_{11}^- \rightleftharpoons H_3F_2^+{\cdot}Sb_2F_{11}^- + H^+{\cdot}Sb_2F_{11}^-$$

$$\Delta\Delta G_1 = -20.4 - (-19.4)\ \text{kcal/mol}$$

$$\Delta\Delta G_1 = -1.0\ \text{kcal/mol}$$

$$H_3F_2^+{\cdot}Sb_2F_{11}^- + H^+{\cdot}Sb_2F_{11}^- \rightleftharpoons H_4F_3^+{\cdot}Sb_2F_{11}^- + Sb_2F_{10}$$

$$\Delta\Delta G_2 = -18.8 - (-20.4)\ \text{kcal/mol}$$

$$\Delta\Delta G_2 = +1.6\ \text{kcal/mol}$$

It is important to point out that the terms shown in the equations above ($H^+{\cdot}Sb_2F_{11}^-$, $H^+{\cdot}SbF_6^-$, etc.) are just shortcut names for the complexes shown in Figure 1 and do not correspond to the naked proton or other isolated species.

From thermodynamics one obtains the following relationships:

$$\Delta\Delta G_1 = -RT\ln K_1 \therefore K_1 = e^{-\Delta\Delta G_1/RT} = \frac{[H_3F_2^+{\cdot}Sb_2F_{11}^-][H^+{\cdot}Sb_2F_{11}^-]}{[H_2F^+{\cdot}Sb_2F_{11}^-]^2}$$

and

$$\Delta\Delta G_2 = -RT\ln K_2 \therefore K_2 = e^{-\Delta\Delta G_2/RT} = \frac{[H_4F_3^+{\cdot}Sb_2F_{11}^-][Sb_2F_{10}]}{[H_3F_2^+{\cdot}Sb_2F_{11}^-][H^+{\cdot}Sb_2F_{11}^-]}$$

and considering

$$[HF]_{total} = [H^+] + [H_2F^+] + [H_3F_2^+] + [H_4F_3^+]$$

where $[HF]_{total}$ is the total amount of HF used to prepare the superacid solution, $[H^+]$ is the concentration of the $H^+{\cdot}Sb_2F_{11}^-$ complex at equilibrium, $[H_2F^+]$ is the concentration of the

Table 1. Reaction Enthalpies, Entropies, and Gibbs Free Energy (298.15 K e 1 atm) for the Equilibria Involving Superacid Species in HF/SbF$_5$, Calculated at the B3LYP/6-31++G**//B3LYP/6-31++G** + RECP(Sb) Level

reaction	ΔH_o (298.15 K) (kcal/mol)	ΔS_o (298.15 K) (cal/mol K)	ΔG_o (298.15 K) (kcal/mol)
$2SbF_5 = Sb_2F_{10}$	−17.7	−43.4	−4.8
$3SbF_5 = Sb_3F_{15}$	−32.3	−82.9	−7.6
$SbF_5 + HF = H^+{\cdot}SbF_6^-$	−8.1	−27.8	+0.2
$H^+{\cdot}SbF_6^- + HF = H_2F^+{\cdot}SbF_6^-$	−13.8	−34.1	−3.6
$H_2F^+{\cdot}SbF_6^- + HF = H_3F_2^+{\cdot}SbF_6^-$	−12.5	−31.4	−3.2
$H_3F_2^+{\cdot}SbF_6^- + HF = H_4F_3^+{\cdot}SbF_6^-$	−11.1	−30.7	−2.0
$Sb_2F_{10} + HF = H^+{\cdot}Sb_2F_{11}^-$	−11.9	−25.3	−4.4
$H^+{\cdot}Sb_2F_{11}^- + HF = 2H^+{\cdot}SbF_6^-$	+13.4	+13.1	+9.5
$H^+{\cdot}Sb_2F_{11}^- + HF = H_2F^+{\cdot}Sb_2F_{11}^-$	−10.1	−32.0	−0.5
$H_2F^+{\cdot}Sb_2F_{11}^- + HF = H_3F_2^+{\cdot}Sb_2F_{11}^-$	−11.6	−34.0	−1.5
$H_3F_2^+{\cdot}Sb_2F_{11}^- + HF = H_4F_3^+{\cdot}Sb_2F_{11}^-$	−13.1	−32.2	−4.1

$H_2F^+{\cdot}Sb_2F_{11}^-$ complex at equilibrium, $[H_3F_2^+]$ is the concentration of the $H_3F_2^+{\cdot}Sb_2F_{11}^-$ complex at equilibrium, and $[H_4F_3^+]$ is the concentration of the $H_4F_3^+{\cdot}Sb_2F_{11}$ complex at equilibrium, it is possible to estimate the concentration of the electrophilic species in the media (molar activities are considered equal to the concentration of the species in this media). After some algebraic manipulation with the equations shown above, it can be shown that

$$[H^+] = [H_3F_2^+] = \frac{\sqrt{K_1}}{2\sqrt{K_1} + \sqrt{K_1K_2} + 1}[HF]_{total}$$

$$[H_2F^+] = \frac{1}{2\sqrt{K_1} + \sqrt{K_1K_2} + 1}[HF]_{total}$$

$$[H_4F_3^+] = [Sb_2F_{10}] = \frac{\sqrt{K_1K_2}}{2\sqrt{K_1} + \sqrt{K_1K_2} + 1}[HF]_{total}$$

The percent amount of each species, related to the total of the ionic species, can be obtained by dividing the concentrations calculated with the above equations by the $[HF]_{total}$, once it was assumed that all the nonprotonated HF would solvate the cations. Using these equations and the values of $\Delta\Delta G_1$ and $\Delta\Delta G_2$ obtained from the DFT calculations, it is possible to estimate the fraction of each cation at the reaction medium, related to the total amount of cation, as

$$\%\ H^+ = [H^+]/[HF]_{total} = 36.9\%$$

$$\%\ H_3F_2^+ = \%\ H^+ = [H_3F_2^+]/[HF]_{total} = 36.9\%$$

$$\%\ H_2F^+ = [H_2F^+]/[HF]_{total} = 16.8\%$$

$$\%\ H_4F_3^+ = [H_4F_3^+]/[HF]_{total} = 9.4\%$$

These results are in agreement with ^{19}F NMR measurements of liquid superacid HF/SbF$_5$ with different molar ratios,[3] which indicate that there is a predominance of the $H_3F_2^+$ cations for 20−40 mol % SbF$_5$. The H_2F^+ concentration of 16.8%, estimated by the DFT calculations for the 1:1 HF:SbF$_5$ solution, is in agreement with the experimental data, which point out that in superacid media with concentrations higher than 40 mol % of SbF$_5$, the $H_3F_2^+$ cations are progressively replaced by the H_2F^+ cation. The crystallographic structure of the 3:2 adduct (33.3 mol % SbF$_5$) indicates that the $H_3F_2^+$ cation is formed and it is associated with the $Sb_2F_{11}^-$ moiety.[6] The experimental bond lengths for the $H_3F_2^+$ cation are shown in Scheme 1a.[6] Figure 2a shows some selected geometrical parameters for the calculated $H_3F_2^+{\cdot}Sb_2F_{11}^-$ complex. It can be observed that the averages of the central H−F bond length (1.163 Å) and the F−F bond length (2.326 Å) agree well with the X-ray results (1.135 and 2.30 Å, respectively, for the terminal F−H and F−F bond lengths; see Scheme 1a).

Table 2. Gibbs Free Energy Changes for the Chemical Equilibria in HF/SbF$_5$ 50 Mol %

equilibrium	ΔG (kcal/mol)
$4SbF_5 + 4HF \rightleftharpoons 4H^+{\cdot}SbF_6^-$	+0.6
$4SbF_5 + 4HF \rightleftharpoons H_2F^+{\cdot}SbF_6^- + SbF_5 + 2H^+{\cdot}SbF_6^-$	−3.1
$4SbF_5 + 4HF \rightleftharpoons 2H_2F^+{\cdot}SbF_6^- + 2SbF_5$	−6.9
$4SbF_5 + 4HF \rightleftharpoons 2H_2F^+{\cdot}SbF_6^- + Sb_2F_{10}$	−11.7
$4SbF_5 + 4HF \rightleftharpoons H_3F_2^+{\cdot}SbF_6^- + 2SbF_5 + H^+{\cdot}SbF_6^-$	−6.5
$4SbF_5 + 4HF \rightleftharpoons H_4F_3^+{\cdot}SbF_6^- + 3SbF_5$	−8.6
$4SbF_5 + 4HF \rightleftharpoons H_3F_2^+{\cdot}SbF_6^- + H^+{\cdot}Sb_2F_{11}^- + SbF_5$	−15.8
$4SbF_5 + 4HF \rightleftharpoons H_2F^+{\cdot}Sb_2F_{11}^- + 2H^+{\cdot}SbF_6^-$	−9.4
$4SbF_5 + 4HF \rightleftharpoons H_3F_2^+{\cdot}SbF_6^- + Sb_2F_{10} + H^+{\cdot}SbF_6^-$	−11.6
$4SbF_5 + 4HF \rightleftharpoons H_4F_3^+{\cdot}SbF_6^- + Sb_3F_{15}$	−16.2
$4SbF_5 + 4HF \rightleftharpoons 2H_2F^+{\cdot}Sb_2F_{11}^-$	−19.4
$4SbF_5 + 4HF \rightleftharpoons H_3F_2^+{\cdot}Sb_2F_{11}^- + H^+{\cdot}Sb_2F_{11}^-$	−20.4
$4SbF_5 + 4HF \rightleftharpoons H_4F_3^+{\cdot}Sb_2F_{11}^- + Sb_2F_{10}$	−18.8
$4SbF_5 + 4HF \rightleftharpoons H_4F_3^+{\cdot}Sb_2F_{11}^- + 2SbF_5$	−13.1

Recently Mootz and Bartmann[6] determined the structure of crystals of HF/SbF$_5$ with a 1:1 molar ratio. They found that the structure actually corresponds to the $H_2F^+{\cdot}Sb_2F_{11}^-$ adduct. In their work it was found that the H_2F^+ has a bent geometry, with a F−H bond length longer than that observed in the free HF molecule. It is also randomly oriented in the crystal. The present calculation shows that the H_2F^+ cation is bent in the $H_2F^+{\cdot}Sb_2F_{11}^-$ complex (Figure 2b). The predicted bond angle is 114.6°.

Un-ionized SbF$_5$, or Sb$_2$F$_{10}$ in solution, has been quoted to be responsible for alkane oxidation[5,13] to the corresponding carbenium ion, in HF/SbF$_5$ solutions with more than 25 mol % SbF$_5$ molar ratios (Scheme 2). NMR studies[3] showed that small amounts of free Sb$_2$F$_{10}$ are present in solutions of HF/SbF$_5$ 50 mol % (1:1 molar ratio). The present calculation shows that about 9% of this species (which would be formed in equimolar quantities to the $H_4F_3^+{\cdot}Sb_2F_{11}^-$ species) could be present in this solution, which is in agreement with the experimental evidence.

Other HF/SbF$_5$ Molar Ratios. Because of how the calculations relate to the electrophilic species present in HF/SbF$_5$

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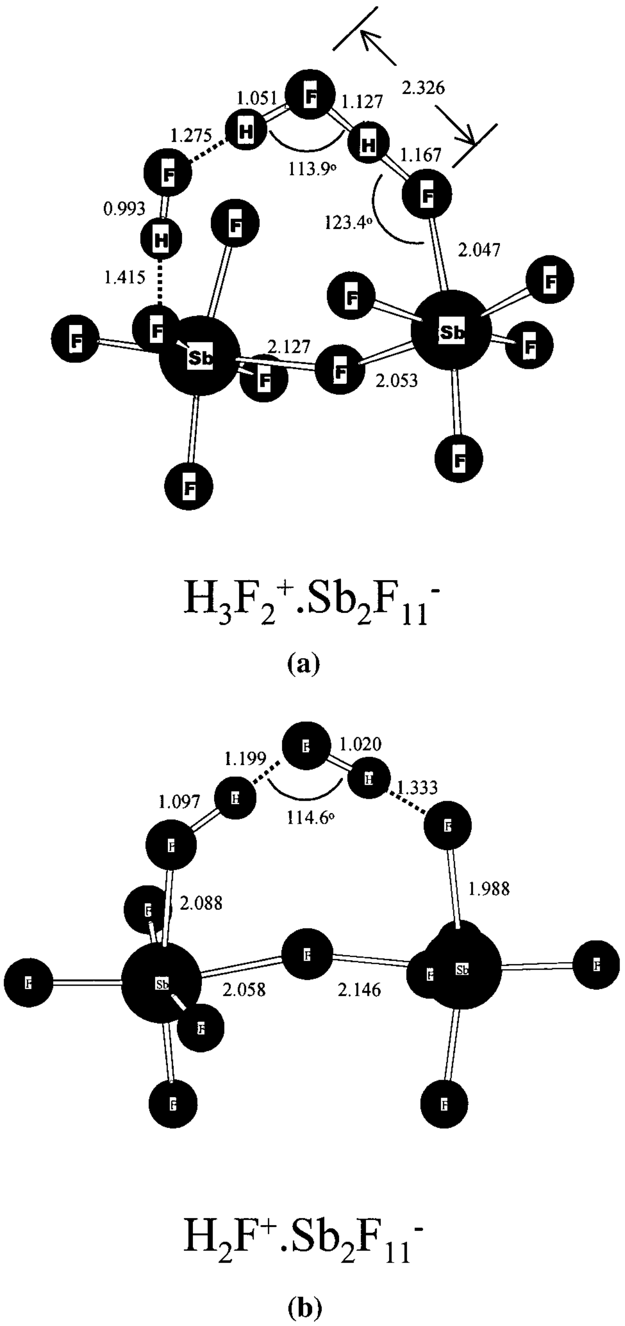
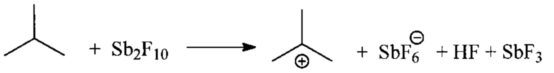


Figure 2. Selected geometrical parameters predicted by the DFT calculations: (a) $H_3F_2^+{\cdot}Sb_2F_{11}^-$ complex and (b) $H_2F^+{\cdot}Sb_2F_{11}^-$.

Scheme 2. Isobutane Oxidation by SbF_5 Dimer



solutions with a 1:1 molar ratio, it is possible to infer trends in solutions with a higher HF/SbF_5 molar ratio. Higher solvation of the electrophilic species seems to be favored when enough free HF molecules are present in the media. Thus, there is some indication from the calculations that the solvated proton $H(HF)_n^+$, with as many HF molecules as possible (higher n values), would be energetically favored. Thus, long chains would be formed, in agreement with experimental[3,4,7] and theoretical predictions.[9] In this case, the first two molecules of HF solvating the proton (first solvation shell) in fact react with this species to form the $H_3F_2^+$ cation, which is then solvated by hydrogen bonding with other HF molecules. Infrared studies of HF/SbF_5 with 0−20 mol % SbF_5 indicate that the predominant species in these media is the $H_3F_2^+$ cation solvated by HF molecules.[4] Mootz and Bartmann elucidated the structure of the adduct SbF_5-$(HF)_7$ (HF/SbF_5 molar ratio 7:1 or 12.6 mol %),[7] where clearly there is a $H_3F_2^+$ cation solvated by four HF molecules (Scheme 1b), which corroborate the trends observed by the DFT calculations. Thus it could be thought that the system, at low HF contents (higher $HF{:}SbF_5$ molar ratio), prefers to form larger associated (polymeric) anions to release HF molecules, which, by its turn, form the most stable (and solvated) cations.

$$2(H_{n+1}F_n)^+{\cdot}SbF_6^- = (H_{n+1}F_n)^+{\cdot}SbF_6^- + (n+1)HF + SbF_5 = (H_{2n+2}F_{2n})^+{\cdot}Sb_2F_{11}^-$$

Acidities of the Different Electrophilic Species. An interesting property to be investigated is the acid strength of each individual electrophilic species shown in Figure 1. Unfortunately this property is difficult to obtain from experimental measurements, since there are many simultaneous equilibria involved. Nevertheless, it is possible to compute the acidity of each species from theoretical data. Acidity is related to the thermodynamics of the following equilibrium:

$$H{-}A = H^+ + A^- \qquad \Delta G_{\text{reaction}} = [\Delta G(H^+) + \Delta G(A^-)] - \Delta G(HA) = -RT\,pK_a$$

Thus, with the knowledge of the structure and energy of the species, it is possible to calculate the acidity. Table 3 reports the thermodynamic data for the deprotonation of the different superacid clusters calculated in this work. As expected, the ΔH for the deprotonation of larger species, with the $Sb_2F_{11}^-$ anion moiety, is lower than the ΔH for the same cation associated to SbF_6^-. This is easily understood if one imagines that there is a larger dispersion of the negative charge in the $Sb_2F_{11}^-$ anion. Thus, this species is expected to be a weaker base than is the SbF_6^-, and consequently its conjugated acid $H_{2n}F_n^+Sb_2F_{11}^-$ is stronger than the parent $H_{n+1}F_n^+$ SbF_6^-. It is interesting to note the great change in entropy for the HF solvated systems. For the SbF_6^- anion, the entropy goes from 13.0 (no solvation by HF) to 42.8 cal/mol K when up to three HF molecules solvate the anion. For the $Sb_2F_{11}^-$ anion, the change goes from 19.8 (no solvating HF) to 44.2 cal/mol K, calculated when three HF molecules solvate the anion. This behavior might be understood if one considers that solvation by HF molecules is more effective for the proton (conjugated acid). Hence, transferring the proton leads to a higher degree of freedom, since the solvating HF molecules are not as well ordered in the anions as they are in the conjugated acid. Therefore, excess HF is more important for stabilizing the conjugated acid than for solvating the anion, which seems to be better stabilized by additional SbF_5 molecules. These data are in agreement with the experimental observation that increasing the SbF_5 content leads to an increase in the acidity. In a series considering the same anion (ca., SbF_6^- or $Sb_2F_{11}^-$), one can see that the enthalpy term (ΔH) increases for more solvated cations. Nevertheless, as we have said before, it is ΔG and not ΔH alone that controls acidity in solution. Entropy favors the more solvated conjugated acid, and at room

Table 3. Reaction Enthalpies, Entropies, and Gibbs Free Energy for the Deprotonation (298.15 K e 1 atm) of Different Electrophilic Species in HF/SbF_5, Calculated at the B3LYP/6-31++G**//B3LYP/6-31++G** + RECP(Sb) Level

equilibrium	ΔH_o (298.15 K) (kcal/mol)	ΔS_o (298.15 K) (cal/mol K)	ΔG_o (298.15 K) (kcal/mol)
$H^+ \cdot SbF_6^- \rightleftharpoons H^+ + SbF_6^-$	260.3	13.0	256.4
$H_2F^+ \cdot SbF_6^- \rightleftharpoons H^+ + HF \cdot SbF_6^-$	261.1	23.0	254.2
$H_3F_2^+ \cdot SbF_6^- \rightleftharpoons H^+ + (HF)_2 \cdot SbF_6^-$ (a)	263.2	37.3	252.1
$H_3F_2^+ \cdot SbF_6^- \rightleftharpoons H^+ + (HF)_2 \cdot SbF_6^-$ (b)	262.1	29.5	253.3
$H_4F_3^+ \cdot SbF_6^- \rightleftharpoons H^+ + (HF)_3 \cdot SbF_6^-$	263.2	42.8	250.4
$H^+ \cdot Sb_2F_{11}^- \rightleftharpoons H^+ + Sb_2F_{11}^-$	251.2	19.8	245.3
$H_2F^+ \cdot Sb_2F_{11}^- \rightleftharpoons H^+ + HF \cdot Sb_2F_{11}^-$	252.7	24.5	245.4
$H_3F_2^+ \cdot Sb_2F_{11}^- \rightleftharpoons H^+ + (HF)_2 \cdot Sb_2F_{11}^-$	253.6	39.8	241.8
$H_4F_3^+ \cdot Sb_2F_{11}^- \rightleftharpoons H^+ + (HF)_3 \cdot Sb_2F_{11}^-$	257.2	44.2	244.1

temperature (298.15 K), this effect is large enough to change the stability order. It is difficult to extrapolate general trends for superacid solutions with the present calculations. However, one can say that the entropy term plays a significant role. The release of solvating HF molecules, upon deprotonation of the superacid complexes, increases the disorder of the system and consequently increases the entropy change (ΔS). Nevertheless, when a base B is present in the medium, the protonated base (HB^+) would probably need solvation from HF. This brings additional complications and eventually can make the enthalpy term predominant in the free energy balance again, governing the equilibrium.

However, the acidity of HF/SbF_5 is found to be at its higher limit ($H_o = -23$) for SbF_5 concentration in the range of 15−20 mol %.[2] This means that for SbF_5 concentration above 20 mol % the rate of protolysis should not increase by increasing the acid strength, but only with the increase of the number of strong acid sites. Hoogeven,[14] on the basis of kinetic measurements, showed that the rate of protonation does not increase linearly with the SbF_5 excess. This could be possibly associated to a second active mechanism for alkane activation, which is the direct alkane oxidation by free SbF_5 (see Scheme 2). This oxidation affords HF, which can further react with the remaining free SbF_5, increasing the number of Brønsted sites. The increase of the number of superacid sites leads to the increase of the overall reaction rate, explaining the deviation from linearity.

IV. Conclusion

In this paper, we reported the structure and energetics of a series of possible electrophilic species present in HF/SbF_5 solutions. The species $H^+ \cdot Sb_2F_{11}^-$, $H_2F^+ \cdot Sb_2F_{11}^-$, $H_3F_2^+ \cdot Sb_2F_{11}^-$, and $H_4F_3^+ \cdot Sb_2F_{11}^-$ were estimated to correspond to 36.9, 16.8, 36.9, and 9.4%, respectively, of the protonic species present in 1:1 HF/SbF_5 solution. For this specific solution it was also predicted that a small amount of free SbF_5 (or Sb_2F_{10}) is formed in approximately an equimolar amount to $H_4F_3^+ \cdot Sb_2F_{11}^-$, in agreement with experimental results. The solvation process of the cationic species seems to be the driving force that governs the several equilibria present in these solutions. In accordance with the expected trend, larger anions ($Sb_2F_{11}^-$) provide more acidic species than do smaller ones (SbF_6^-). However, increasing the solvation of the cations containing the same anion (e.g., $H^+ \rightarrow H_4F_3^+ \cdot A^-$, $A^- = SbF_6^-$ or $Sb_2F_{11}^-$) increases the ΔH. Entropy changes (ΔS) also play a decisive role in the reverse direction. The more solvated ions afford a more disorganized species upon deprotonation (larger ΔS). This has consequences in the ΔG, which is driven by the entropic term at 298.15 K. Nevertheless, the nature of the solvation of the base in this media can change the contribution of the entropic term.

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Supporting Information Available: Table including absolute energies, ZPE, thermal corrections to 298.15 K and 1 atm, and absolute entropies for the species in HF/SbF_5 media and related molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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