Gas-Phase Acidities of Some Neutral Brønsted Superacids: A DFT and ab Initio Study

Ilmar A. Koppel,*[†] Peeter Burk,[†] Ivar Koppel,[†] Ivo Leito,[†] Takaaki Sonoda,[‡] and Masaaki Mishima[§]

Contribution from the Institute of Chemical Physics, Department of Chemistry, University of Tartu, Jakobi 2, 51014 Tartu, Estonia, and Institute of Advanced Material Science, Kyushu University, Kasuga 816, Japan, and Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan

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Abstract: For the first time G2 or G2(MP2) calculations or both have been performed to calculate the acidity and deprotonation enthalpy of classical strong mineral acids $HClO_4$, CF_3SO_3H, FSO_3H, H_2SO_4, HBF_4, HPO_3, and HNO_3. Also, the intrinsic acidities and gas-phase deprotonation enthalpies for 39 neutral strong or superstrong Brønsted acids, Brønsted−Lewis conjugate acids, and some compounds modeling the acidic clusters of zeolites were calculated using the DFT B3LYP 6-311+G** approach. DFT B3LYP method at 6-31+G* basis was used for the calculation of the intrinsic Brønsted acidities of the conjugate acids of the carborane anion $CB_{11}H_{12}^-$ and its mono-, hexa-, and dodecafluorinated analogues. G2 and G2(MP2) theories describe the acidities of different compounds better than DFT B3LYP//6-311+G**. However, the DFT results could also be used for the estimation of the acidity of compounds which are out of reach of G2 or G2(MP2) theory. The estimated ΔG_{acid} values obtained this way can be used as the substitutes for the unavailable experimental values, especially for those (rather numerous) compounds for which the experimental determination of ΔG_{acid} is very difficult. In the case of practically all considered families of compounds extremely high acidities (low ΔG_{acid} values) could be reached. If the compounds were started from HF as the parent acid, then the estimated ΔG_{acid} as low as 249.0 kcal/mol (for $F(OSO_2)_4H$) could be reached by formation of Brønsted−Lewis conjugate acids by consecutive complexation with SO_3 molecules. Also very low ΔG_{acid} value ($\Delta G_{\text{acid}}(HSbF_6) = 255.5$) could be reached by complexation of HF with SbF_5. At least as high intrinsic acidities as in case of the strongest Brønsted−Lewis superacids could be reached in the case of progressive introduction of highly electronegative, correctly oriented polarizable dipolar electron-accepting substituents into the acidity site. Indeed, the introduction of five CN groups into cyclopentadiene is expected to lead to the acidity $\Delta G_{\text{acid}} = 250.1$ kcal/mol which is lower than the corresponding quantity even for hexafluoroantimonic acid ($\Delta G_{\text{acid}} = 255.5$ kcal/mol). However, by far the strongest intrinsic Brønsted acidity ($\Delta G_{\text{acid}} = 209$ kcal/mol) for dodecafluorosubstituted carborane acid $CB_{11}F_{12}H$ is predicted to exceed the intrinsic acidity of sulfuric acid by about 90 kcal/mol or by almost 70 powers of ten, whereas semi-empirical PM3 calculations suggest that the conjugate acid of the dodecatrifluoromethylmonocarborane anion $CB_{11}(CF_3)_{12}^-$ could be the first neutral Brønsted superacid whose acidity (deprotonation energy) is expected to be below the landmark 200 kcal/mol level. An approximate linear relationship is found to hold between the calculated gas-phase acidities of strong and superstrong Brønsted acids and the corresponding Hammett acidity functions of the corresponding neat acids. The simultaneous existence of the widely overlapping areas on the gas-phase acidity scale of neutral and cationic Brønsted acids evidences strongly for the feasibility of the spontaneous proton-transfer equilibria between neutral Brønsted acids and bases.

Introduction

Superacids are acid systems[1−6] that are more acidic than conventional strong mineral Brønsted acids. According to Gillespie's arbitrary but widely accepted definition[7] superacids are acid systems whose acidity exceeds that of 100% sulfuric acid, that is, $H_0 < -12$.

Liquid and solid superacids of different origin (Brønsted and Lewis superacids or conjugate Brønsted−Lewis superacids, see ref 1 for the classification) have been created. Some of those systems, particularly the conjugate Brønsted−Lewis superacids (e.g., $HF-SbF_5$, FSO_3SbF_5H, etc.) are by their liquid-phase superacidity ($H_0 < -30$) more than 18 powers of 10 stronger than 100% H_2SO_4. Most of the large variety of the superacidic systems and various derivatives of superacids are of great

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* Author for correspondence.Telephone: (+372-7) 375 263. Fax (+372-7) 375 264. E-mail: ilmar@chem.ut.ee.

[†] University of Tartu.

[‡] Institute of Advanced Material Science, Kyushu University.

[§] Institute for Fundamental Research of Organic Chemistry, Kyushu University.

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importance in different fields of organic synthesis and petrochemical applications,[8−15] electrochemical technologies (fuel cells,[16] lithium batteries,[17,18] electric double-layer capacitors[19]), etc.

The acidities of the liquid Brønsted or conjugate Brønsted−Lewis superacidic systems have been obtained or estimated using different experimental techniques (UV−Vis, NMR, kinetic methods, etc.).[1,20−23]

Due to substantial experimental and theoretical difficulties, well-defined pK_a values of strongly acidic components (e.g., FSO_3H, CF_3SO_3H, H_2SO_4, $HClO_4$, HBF_4, etc.) are not available for the aqueous solution, and in some cases the uncertainties of those values exceed several powers of 10.[24,25]

The situation is somewhat better for the nonaqueous solutions (e.g., DMSO,[26] CH_3CN[27,28]) or the gas phase[25,29] as standard state for such measurements. Gas-phase acidities (GA) of a neutral acid HA and proton affinities (PA(A^-)) of the anionic base A^- refer to the following equilibrium:

$$\mathrm{HA} \xrightleftharpoons{\Delta G,\, \Delta H} \mathrm{H}^+ + \mathrm{A}^- \qquad (1)$$

where $\Delta G_{\mathrm{acid}} \equiv \mathrm{GA} \equiv \Delta G$ and $\Delta H_{\mathrm{acid}} \equiv \mathrm{PA}(\mathrm{A}^-) \equiv \Delta H$. By definition, the gas-phase acidity of a neutral acid HA is equal to the gas-phase basicity toward the proton of its conjugate anion, A^-. These quantities are of fundamental interest, and they provide valuable information about the inherent (intrinsic), solvent-independent properties of the acids. Recently, an extensive equilibrium scale of intrinsic gas-phase acidities of a large number of very strong Brønsted acids was established using the FT-ICR technique.[25] This particular scale lists the intrinsic acidities of more than 20 CH, NH, and OH acids which are by their absolute acidity stronger than H_2SO_4. At the same time the flowing afterglow technique has made available the gas-phase acidities of HPO_3, H_2SO_4, and FSO_3H.[29,30] By using a selected ion flow tube, an additional gas-phase acidity value for CF_3SO_3H ($\Delta G_{\mathrm{acid}} = 298.8$ kcal/mol) is available.[30a] However, several important questions remain unanswered.

Due to the experimental problems, the acidities of perchloric acid and chlorosulfonic acid were never measured in the gas-phase.[25] The earlier estimates by one of us[31] and recent calculations[32] (DFT and MP2/6-311++G**/6-31+G*, frozen core approximation) predict the gas-phase acidity of $HClO_4$ somewhere in the range between 275 and 300 kcal/mol. The value, preferred by the NIST tables is 281 ± 15 kcal/mol.[29] Attempts to measure the acidity of $ClSO_3H$ by FT-ICR have thus far failed.[25] In a recent work[32] its deprotonation energy value is estimated to be (DFT/6-31+G* (292.7 kcal/mol), MP2/6-311++G**/6-31+G* (296.6 kcal/mol)) around 295 ± 3 kcal/mol which means that $ClSO_3H$ is predicted to be a stronger acid in the gas phase than FSO_3H. Also, a long-standing question is whether FSO_3H and CF_3SO_3H are stronger or weaker acids in the gas phase than perchloric acid. The H_0 function of the neat FSO_3H is −15.1,[1] for CF_3SO_3H −14.1,[1] for the neat $ClSO_3H$ −13.8,[1] and for the neat $HClO_4$ ∼ −13.0.[1] The ab initio (MP2/6-311++G**//3-21G*) and DFT (B88-LYP/DNP, 6-31+G* basis set) study predicts that FSO_3H, CF_3SO_3H, and $HClO_4$ acids are of similar strength: their DFT/DNP deprotonation energies are given in a rather narrow range from 296.6 (FSO_3H) to 301.8 ($HClO_4$) kcal/mol. The DFT/DNP (B88-LYP/DNP) ΔG_{acid} value 291.0 kcal/mol for trifluoromethanesulfonic acid is estimated.[32] Available experimental gas-phase data indicate that trifluoromethanesulfonic acid is approximately of the same strength ($\Delta G_{\mathrm{acid}} = 299.5$) as fluorosulfonic acid ($\Delta G_{\mathrm{acid}} = 299.8$).

According to the rough and partially indirect experimental evidence, several polycyanocarbon acids (e.g., cyanoform, $(CN)_2C{=}C(CN)CH(CN)_2$, pentacyanocyclopentadiene, etc.) are expected to exhibit probably even stronger acidic properties than those classical superstrong mineral acids.[33,34] However, the attempts to measure their inherent gas-phase acidity have thus far failed.[25] Estimates, which reach acidity as high as <-11 pK_a units (≥ 27 pK_a units more acidic than the unsubstituted cyclopentadiene (p$K_a = 16.0$) in aqueous solution), have been cited[34] for aqueous solution. Even more so, it was found that pentacyanocyclopentadienide anion is a base so weak that it is not protonated even in the Magic Acid.[34]

Also, the intrinsic acidity of the (main) components of conjugate Brønsted−Lewis superacids such as oleum (pyrosulfuric or disulfuric acid $H_2S_2O_7$, trisulfuric acid $H_2S_3O_{10}$), hexafluoroantimonic acid ($HSbF_6$), hexafluorotantalic acid ($HTaF_6$), tetrafluoroboric acid (HBF_4), $HAlCl_4$, $HAlBr_4$, Magic Acid (FSO_3SbF_5H), hexafluorophosphoric acid (HPF_6), fluo-

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ropyrosulfuric acid ($F(SO_3)_2H$), fluorodipyrosulfuric acid ($F(SO_3)_3H$), trifluoromethylpyrosulfuric acid ($CF_3(SO_3)_2H$) was never experimentally studied in the gas phase. At the same time, as indicated by their Hammett acidity function values (vide supra), several of those superacid systems display extraordinarily high acidity: for example, the H_0 value for some ratios of HF and SbF_5 is ≤ -30,[1] the H_0 value for the Magic Acid reaches as low as -26.5,[1] for oleum ~ -14.5,[1] HBF_4 -16.6,[20,21,23] $HTaF_6$ -18.9, $HAlCl_4$ ~ -15,[1,35] $F(SO_3)_2H$ -15.5[1], etc.

The practical demands[16−19] and fundamental challenges—attempts to prepare unstable cations, superstrong oxidants, etc.—have stimulated the still ongoing endeavor for creating the least coordinating, extremely weak nucleophilic anions,[44−46] for example, tetraphenylborate, perfluorotetraphenylborate, tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate, $OTeF_5^-$, $(CF_3SO_2)_2N^-$, derivatives of 1-carba-*closo*-dodecaborate ion, and especially its 7,8,9,10,11,12-hexahalogenoderivatives $CB_{11}H_6X_6^-$ (X = F,[36,37,38] Cl,[39,40] Br,[39,41,42] I[40]) and undecahalogenoderivatives $1\text{-H}-CB_{11}F_{11}^-$,[37] $1\text{-CH}_3-CB_{11}F_{11}^-$,[37] and $1\text{-CH}_3-CB_{11}Cl_{11}^-$.[40] Also, the design and study of derivatives of $CB_9H_{10}^-$ is under way[42] (see refs 36−43 and reviews 44−47 for further literature sources). In principle, the design of different other representatives of extra-weakly coordinating anions of the carborane family seems possible via the multiple introduction of different strongly electronegative and weakly coordinating groups (e.g., CF_3) into $CB_{11}H_{12}^-$.

Different, rather specific probes (see, e.g., refs 44−46) have been used for estimation of the coordinating ability or nucleophilicity of those superweakly coordinating anions. However, the affinity of the latter toward a superelectrophile—proton—has never been quantitatively estimated.

Assuming some parallelism between the low coordinating ability and nucleophilicity of the anion on one hand and the high intrinsic Brønsted acidity of its conjugate acid on the other hand, one might expect that $CB_{11}H_{12}H$ and its derivatives can display quite extraordinary superacidic properties. To the best of our knowledge, this question has not yet been the object of serious theoretical investigation. To partially fill this gap, the problem of calculation of the intrinsic gas-phase acidity of some conjugate acids of some monocarborane anions is undertaken in this work. In practice, the striking evidence of potential superstrong Brønsted acidity of hexachlorosubstituted carborane acid $CB_{11}H_6Cl_6H$ was very recently given by preparation and isolation its salts with simple arenes, including benzene.[41] Also, as the first example of ambiently stable salt of hydroxonium ion, the salt $[H_9O_4]^+$ $[CB_{11}H_6Br_6]^-$ has been isolated.[42]

There are no general methods of unambiguous experimental determination (evaluation) of the intrinsic Brønsted acidity of acid sites of strong solid-state acids, in particular, of zeolites.[4−6] Traditionally zeolites have been considered superacids,[1] but there is also strong evidence in favor of zeolites being not as acidic as often believed.[5] The indirect evidence (FT-IR, FT-NMR, calorimetry, etc.) and theoretical modeling of the Brønsted acid site clusters for different acidic zeolites, place the intrinsic acidity of zeolites into a rather wide range between 275 and 325 kcal/mol.[4−6,48−52]

Preliminary information about the relative gas-phase strength of a few of the above-mentioned superacids has been obtained from recent[32] ab initio or DFT calculations. However, these calculations have been performed using different (sometimes rather modest: e.g., HF 6-31G**) levels of theory (different levels of optimization of the geometry and calculation of energetics of the molecules and ions). Therefore, those results are not strictly comparable to each other. Usually only the deprotonation energies, corrected for zero-point energies, are calculated. No calculations of gas-phase acidities (ΔG_{acid}) are performed. Also, to the best of our knowledge, those calculations are not yet supported at the highest levels of theory, for example, G2 or G2(MP2) theory.

Among the major goals of this investigation were to calculate at the G2 or G2(MP2) level of theory the gas-phase acidities of most widespread conventional strong Brønsted acids CF_3SO_3H, $HClO_4$, H_2SO_4, FSO_3H, HBF_4, HPO_3, and HNO_3 and to provide a systematic computational study of those and other above-mentioned Brønsted superacids and Brønsted−Lewis conjugate acids using the density functional theory (DFT) approach with the Becke3-LYP hybrid functional and the 6-311+G** basis set (6-31+G* basis set for the carborane acids).

Computational Details

The high level ab initio and DFT computations reported in this work were carried out using Gaussian94 and Gaussian98 series of programs[53] on IRIX based SGI Origin 200 workstations and on HPC-Alpha164 workstations. Some of the HF/3-21G(*) and PM3 calculations were carried out on a DEC Brain PC using PC Spartan V1.0.1.

Ab initio calculations of some superacids (vide supra) were performed using G2 and G2(MP2) theory which effectively corresponds to the quadratic configuration interaction quadratic configuration interaction (QCISD(T)) with 6-311+G(3df, 2p) basis set, uses MP2-

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Table 1. Results of Acidity Calculations at G2 and G2(MP2) Level Together with the Available Experimental Data

acid	AH[a]			A^- ta			ΔH[b]	ΔG[b]	exp[b]	sc[b]
	E	H	G	E	H	G				
					G2					
H_2SO_4	−699.4874	−699.4812	−699.5150	−698.9930	−698.9871	−699.0217	311.5	303.3	302.2	
FSO_3H	−723.5002	−723.4945	−723.5282	−723.0220	−723.0168	−723.0486	301.3	294.7	299.8	
HNO_3	−280.5588	−280.5544	−280.5844	−280.0449	−280.0408	−280.0686	323.8	317.4	317.8	
HPO_3	−567.0076	−567.0026	−567.0343	−566.5138	−566.50928	−566.5386	311.0	304.8	303.3	
$HClO_4$	−760.5916	−760.5857	−760.6195	−760.1160	−760.1110	−760.1410	299.4	294.0		
HBF_4	−424.5907	−424.5831	−424.6216	−424.1266	−424.1212	−424.1519	291.3	288.5		
					G2(MP2)					
H_2SO_4	−699.4734	−699.4672	−699.5010	−698.9780	−698.9721	−699.0067	312.2	303.9	302.2	303.4
FSO_3H	−723.4854	−723.4797	−723.5134	−723.0059	−723.0008	−723.0325	302.0	295.4	299.8	295.0
CF_3SO_3H	−961.0134	−961.0048	−961.0462	−960.5375	−960.5296	−960.5687	299.8	293.3	299.5	292.9
HNO_3	−280.5501	−280.5457	−280.5757	−280.0347	−280.0306	−280.0584	324.7	318.4	317.8	317.8
HPO_3	−566.9979	−566.9929	−567.0247	−566.5032	−566.4987	−566.5297	311.6	304.3	303.3	304.1
$HClO_4$	−760.5771	−760.5714	−760.6052	−760.1000	−760.0950	−760.1250	300.5	295.0		294.6
HBF_4	−424.5770	−424.5693	−424.6079	−424.1115	−424.1061	−424.1368	292.2	289.3		288.9

[a] G2 and G2(MP2) energies (E, at 0 K), enthalpies (H, at 298.15 K) and Gibbs free energies (G, at 298.15 K). The values are in Hartrees. [b] ΔH_{acid} values (ΔH), ΔG_{acid} values (ΔG), experimental ΔG_{acid} values (exp), and scaled ΔG_{acid} values (sc; for G2(MP2) only) given in kcal/mol (1 cal = 4.184 J).

(full)/6-31G(d) optimized geometries, and incorporates scaled (0.8929) HF/6-31G(d) zero-point energies and so-called "higher-level correction" term.

DFT calculations were performed using B3LYP hybrid functional, which has been proved[54−58] to be reliable in the study of energetics and geometrical properties of the proton transfer and other ion−molecule reactions. As a rule, full geometry optimizations and vibrational analyses were performed using the 6-311+G** basis set. All stationary points were found to be true minima (number of imaginary frequencies, N_{imag}, = 0). Thermodynamic quantities ΔG_{acid} and ΔH_{acid} (at 298 K) were calculated using standard procedures taking into account zero-point energies, finite temperature (0 to 298 K) correction, and the pressure−volume work term pV.

The intrinsic acidity of the unsubstituted carborane acid $CB_{11}H_{12}H$ and its 12-fluoro ($CB_{11}H_{11}FH$), 7,8,9,10,11,12-hexafluoro ($CB_{11}H_6F_6H$), and perfluoro ($CB_{11}F_{12}H$) derivatives were calculated at DFT B3LYP level using a somewhat smaller 6-31+G* basis. The acidity of the parent compound, $CB_{11}H_{12}H$, was calculated also at the DFT B3LYP/6-311+G** level. The comparison of deprotonation energies of carborane acids $CB_{11}H_{11}FH$, $CB_{11}H_6X_6H$ (X = F, Cl, Br, CN) and $CB_{11}X_{12}H$ (X = F, Cl) has been done at ab initio 3-21G* level of theory. The same calculations with the additional inclusion of $CB_{11}H_6(CF_3)_6H$, $CB_{11}(CN)_{12}H$, $CB_{11}(CF_3)_{12}H$, $CB_{11}H_6(SO_2CF_3)_6H$ and $CB_{11}(SO_2CF_3)_{12}H$ were performed also using semiempirical PM3 method.

The geometries of all of the acids and anions discussed in this work are available from the authors on request.

Results and Discussion

The resulting G2, G2(MP2), and B3LYP/6-311+G** total energies, corrected to 298 K enthalpies and Gibbs' free energies and calculated gas-phase acidities of acids HA and proton affinities of anions A^- are given in Tables 1 and 2 respectively, along with the $(\Delta G_{acid})_{calc}$ values and the corresponding scaled quantities, $(\Delta G_{acid})_{Sc}$ (vide infra). The results of calculations of intrinsic acidities and deprotonation energies of some representatives of the carborane family are included in Tables 3 and 4.

G2 and G2(MP2) Calculations. The results of the G2 and G2(MP2) calculations from Table 1 support the following intrinsic acidity order for the strong Brønsted acids: $HNO_3 < HPO_3 < H_2SO_4 < CF_3SO_3H < FSO_3H < HClO_4 < HBF_4$. At G2(MP2) level all of the classical widely used strong acids (H_2SO_4, HPO_3, CF_3SO_3H, FSO_3H, and $HClO_4$) are in a relatively narrow acidity range $(\Delta\Delta G_{acid})_{calc} = 12.6$ kcal/mol. At the same time, at G2(MP2) level FSO_3H is found to be a somewhat weaker acid (by 2.1 kcal/mol) than trifluoromethanesulfonic acid. In its turn, perchloric acid is predicted at G2(MP2) level to be a slightly stronger acid (by 0.4 kcal/mol) than fluorosulfonic acid. At G2 level perchloric acid has the calculated ΔG_{acid} value 294.0 kcal/mol which helps to end the longstanding uncertainty about the most probable value of the intrinsic acidity of this acid. The difference between $(\Delta G_{acid})_{calc}$ and $(\Delta G_{acid})_{exp}$ is within 1−2 kcal/mol for H_2SO_4, HNO_3, and HPO_3, whereas the calculated and measured values for fluorosulfonic and trifluoromethanesulfonic acid differ by 4−5 kcal/mol. For the latter compound the ΔG_{acid} value (293.3 kcal/mol) calculated using G2(MP2) theory is closer to the experimentally determined values than the DFT(B88-LYP/DNP) value from ref 32.

Recently, the performance of G2(MP2) theory in reproducing the experimental intrinsic acidity ΔG_{acid} values for a wide range of different Brønsted acids covering the range of almost 100 kcal/mol with $318.0 \leq \Delta G_{acid} \leq 410.4$ kcal/mol was evaluated by the present authors.[59] An approximate linear scaling equation $(\Delta G_{acid})_{calc} = a(\Delta G_{acid})_{exp} + b$ with close to the unity slope ($a = 1.008 \pm 0.014$) and practically zero intercept ($b = -1.9 \pm 5.2$) was found to hold ($r^2 = 0.997$ $s = 1.4$). The use of this equation for the results of the present G2(MP2) calculations for conventional strong Brønsted acids from Table 1 leads to the scaled experimental ΔG_{acid} values at 298 K that are less than the directly calculated ΔG_{acid} values by a rather constant increment, ~0.4 kcal/mol. Scaling of computational results is generally undesirable.[54] The values that are obtained are dependent on the set of compounds used to set up the scaling equation and are therefore not uniquely determined. However, to get the most probable estimates of the experimental values for the acids for which direct experimental measurement of acidity is very complicated, we decided to include also the scaled data in Table 1.

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Table 2. Results of Acidity Calculations at DFT B3LYP 6-311+G** Level Together with the Available Experimental Data

	AH^a			$A^{-\ ta}$						
acid	E	H^b	G^b	E	H^b	G^b	$\Delta H^{b,c}$	$\Delta G^{b,c}$	$\exp^{b,c}$	$sc^{b,c}$
H_2SO_4	−700.3390	−700.2946	−700.3291	−699.8367	−699.8046	−699.8390	309.0	301.2	302.2	306.0
$H_2S_2O_7$	−1324.2094	−1324.1465	−1324.1914	−1323.7511	−1323.7004	−1323.7444	281.4	274.2		280.2
$H_2S_3O_{10}$	−1948.0719	−1947.9907	−1948.0478	−1947.6331	−1947.5640	−1947.6217	269.3	261.0		267.7
FSO_3H	−724.3582	−724.3261	−724.3600	−723.8744	−723.8546	−723.8868	297.4	290.6	299.8	295.9
$F(SO_3)_2H$	−1348.2203	−1348.1697	−1348.2156	−1347.7691	−1347.7308	−1347.7772	276.9	268.8		275.1
$F(SO_3)_3H$	−1972.0802	−1972.0131	−1972.0708	−1971.6482	−1971.5915	−1971.6514	266.0	256.9		263.7
$F(SO_3)_4H$	−2595.9459	−2595.8586	−2595.9264	−2595.5214	−2595.4464	−2595.5196	260.1	249.0		256.2
CF_3SO_3H	−962.2167	−962.1698	−962.2116	−961.7304	−961.6958	−961.7355	298.3	292.5	299.5	297.7
$CF_3(SO_3)_2H$	−1586.0801	−1586.0147	−1586.0684	−1585.6248	−1585.5717	−1585.6257	279.5	271.5		277.7
HPO_3	−567.7606	−567.7328	−567.7648	−567.2576	−567.2420	−567.2715	309.5	303.2	303.3	307.9
H_3PO_4	−644.2807	−644.2253	−644.2615	−643.7535	−643.7100	−643.7447	324.9	318.0		322.0
$H_4P_2O_7$	−1212.1063	−1212.0205	−1212.0671	−1211.6108	−1211.5377	−1211.5849	304.5	296.3		301.3
$ClSO_3H$	−1084.7078	−1084.6766	−1084.7122	−1084.2296	−1084.2105	−1084.2445	294.0	287.2		292.6
$HClO_4$	−761.4183	−761.3864	−761.4212	−760.9324	−760.9133	−760.9437	298.4	293.3		298.5
CH_3SO_3H	−664.4247	−664.3567	−664.3936	−663.9066	−663.8509	−663.8853	318.9	312.7	315.0	317.0
HBF_4	−425.1508	−425.1202	−425.1599	−424.9797	−424.6606	−424.6914	289.9	287.7		293.1
HPF_6	−941.3466	−941.3099	−941.3565	−940.8966	−940.8712	−940.9057	276.8	276.6		282.5
$HSbF_6$	−605.3596	−605.3262	−605.3729	−604.9376	−604.9155	−604.9558	259.2	255.5		262.4
$HTaF_6$	−657.0576	−657.0235	−657.0696	−656.6148	−656.5925	−656.632	271.8	268.3		274.6
$HAlCl_4$	−2084.1840	−2084.1614	−2084.2070	−2083.7609	−2083.7472	−2083.7866	261.5	257.4		264.2
$HAlBr_4$	−10539.8581	−10539.8368	−10539.8877	−10539.4354	−10539.4222	−10539.4671	261.6	257.6		264.4
FSO_3SbF_5H	−1229.0382	−1228.9843	−1229.0376	−1228.6168	−1228.5751	−1228.6285	255.3	250.4		257.5
$HC(CN)_3$	−317.2778	−317.2274	−317.2647	−316.7986	−316.7605	−316.7963	294.5	287.6		293.0
$(CN)_2C{=}C(CN)CH(CN)_2$	−579.2103	−579.1237	−579.1771	−578.7630	−578.6888	−578.7412	274.3	267.2		273.6
$HC(NO_2)_3$	−654.1638	−654.0997	−654.1445	−653.6699	−653.6188	−653.6645	303.3	294.9		300.0
$HC(SO_2F)_3$	−1984.2091	−1984.1403	−1984.1961	−1983.7217	−1983.6651	−1983.7204	299.7	292.2		297.4
$HC_5(CN)_5$	−655.4459	−655.3464	−655.4012	−655.0278	−654.9399	−654.9926	256.6	250.1		257.3
$HN(SO_2F)_2$	−1352.3744	−1352.3233	−1352.3688	−1351.9030	−1351.8650	−1351.9088	289.1	282.4		288.0
$H_2C(SO_2F)_2$	−1336.3383	−1336.2756	−1336.3206	−1335.8375	−1335.7884	−1335.8340	307.2	299.0	307.3	303.9
$CF_3SO_2CH(CN)_2$	−1110.7823	−1110.7111	−1110.7636	−1110.3115	−1110.2526	−1110.3039	289.3	282.2		287.9
H1	−611.4665	−611.3976	−611.4358	−610.9674	−610.9118	−610.9511	306.3	297.8		302.8
OH1	−1063.3592	−1063.2429	−1063.2974	−1062.8624	−1062.7581	−1062.8125	305.7	298.0		303.0
F1	−1207.5723	−1207.5278	−1207.5770	−1207.1370	−1207.1037	−1207.1553	267.6	258.3		265.1
H2	−977.5480	−977.4521	−977.5022	−977.0550	−976.9721	−976.0242	302.7	293.6		298.5
2H2	−1297.1326	−1297.0032	−1297.0605	−1296.6466	−1296.5304	−1296.5883	298.2	290.0		295.3
CF_3COOH	−526.9655	−526.9197	−526.9586	−526.4448	−526.4124	−526.4519	319.8	311.7	316.3	316.0
CF_3COSH	−849.9177	−849.8770	−849.9174	−849.4067	−849.3762	−849.4162	315.8	308.2	312.5	312.7
HNO_3	−280.9786	−280.9478	−280.9781	−280.4575	−280.4396	−280.4676	320.4	314.0	317.8	318.2
$CB_{11}H_{12}H$	−319.4971	−319.3068	−319.3495	−319.0572	−318.8768	−319.9164	271.3	265.5		271.9

[a] HF energies at 0 K without ZPV corrections (*E*), enthalpies (*H*), and Gibbs free energies (*G*). The values are in Hartrees. [b] Values at 298 K. [c] ΔH_{acid} values (ΔH), ΔG_{acid} values (ΔG), experimental ΔG_{acid} values (exp), and scaled ΔG_{acid} values (sc) given in kcal/mol (1 cal = 4.184 J).

Table 3. Results of DFT B3LYP 6-31+G* Calculations of Carborane Acids and Anions

species	protonation site^a	E^b	$H^{b,c}$	$G^{b,c}$	$\Delta H^{c,d}$	$\Delta G^{c,d}$
$CB_{11}H_{12}^-$		−319.0080	−318.8265	−318.8659		
$CB_{11}H_{12}H$	$B_{12}{}^e$	−319.4413	−319.2510	−319.2910	267.8	260.4
$CB_{11}H_{12}H$	7−8−12^f	−319.4373	−319.2461	−319.2864	*264.8*	*257.6*
$CB_{11}H_{12}H$	2−7−8	−319.4278	−319.2371	−319.2776	*259.1*	*252.1*
$CB_{11}H_{12}H$	2−3−7	−319.4293	−319.2382	−319.2785	*259.9*	*252.6*
$CB_{11}H_{11}F^-$		−418.3103	−418.1344	−418.1761		
$CB_{11}H_{11}FH$	F_{12}	−418.7128	−418.5257	−418.5709	*247.0*	*241.5*
$CB_{11}H_{11}FH$	7−8−12	−418.7301	−418.5446	−418.5874	258.8	251.9
$CB_{11}H_6F_6$-		−914.7942	−914.6466	−914.6996		
$CB_{11}H_6F_6H$	$F_{12}\rightarrow F_7$	−915.1759	−915.0175	−915.0710	*234.3*	*226.8*
$CB_{11}H_6F_6H$	7−8−12	−915.1801	−915.0229	−915.0777	237.6	231.0
$CB_{11}F_{12}$-		−1510.4803	−1510.3687	−1510.4357		
$CB_{11}F_{12}H$	$F_{12}\rightarrow F_7{}^g$	−1510.8333	−1510.7116	−1510.7791	216.7	209.2
$CB_{11}F_{12}H$	7−8−12	−1510.8294	−1510.7090	−1510.7780	*215.0*	*208.5*

[a] The site of protonation for the protonated forms. X−Y−Z denotes structure, protonated on the surface in the center of the triangle specified by X, Y, and Z; $A_X \rightarrow B_Y$ denotes structure protonated on substituent A in the position X and giving hydrogen bond to substituent B in position Y. [b] HF energies at 0 K without ZPV corrections (*E*), enthalpies (*H*), and Gibbs free energies (*G*). The values are in Hartrees. [c] Values at 298 K. [d] ΔH_{acid} values (ΔH), and ΔG_{acid} values (ΔG) given in kcal/mol (1 cal = 4.184 J). The valid estimates are the nonitalicized values corresponding to the most stable protonated forms. [e] Protonated on the boron B12. B12 bears two symmetrically arranged hydrogens (see also Figure 2a). [f] See Figure 2b. [g] See Figure 2c.

DFT B3LYP 6-311+G Calculations.** As far as the comparisons between the predictions of G2 and G2(MP2) approach and DFT B3LYP 6-311+G** calculations are available (See Table 2, H_2SO_4, HNO_3, CF_3SO_3H, FSO_3H and $HClO_4$, HPO_3, HBF_4), the qualitative acidity orders are mostly the same. However, in contrast to G2(MP2) theory, the DFT B3LYP 6-311+G** approach predicts the trifluoromethanesulfonic acid to be by 1.9 kcal/mol weaker than fluorosulfuric acid.

The classical strong mineral acids (e.g., HNO_3, HPO_3, H_3PO_4, H_2SO_4, $HClO_4$, FSO_3H, CF_3SO_3H) are predicted to have

Table 4. Results of PM3 and HF 3-21G* Estimation of ΔH_{acid} and ΔG_{acid} Values of Various Carborane Acids

		PM3	HF 3-21G*	
acid	protonation site[a]	ΔH_{acid}[b]	ΔH_{acid}[b]	ΔG_{acid}[b]
$CB_{11}H_{12}H$	B_{12}[c]	292	260	255
$CB_{11}H_{11}FH$	7−8−12[d]	266	248	242
$CB_{11}H_6F_6H$	7−8−12[e]	246	234	226
$CB_{11}H_6Cl_6H$	$Cl_{12}\rightarrow Cl_7$	261	237	230
$CB_{11}H_6Br_6H$	$Br_{12}\rightarrow Br_7$	222	236	229
$CB_{11}H_6(CN)_6H$	$(CN)_{12}$	263	262	255
$CB_{11}H_6(CF_3)_6H$	$(CF_3)_{12}\rightarrow(CF_3)_7$	221	–	–
$CB_{11}H_6(SO_2CF_3)_6H$	$Tf_{12}\rightarrow Tf_7$[f]	260	–	–
$CB_{11}F_{12}H$	$F_{12}\rightarrow F_7$	229	211	205
$CB_{11}Cl_{12}H$	$Cl_{12}\rightarrow Cl_7$	247	222	215
$CB_{11}(CN)_{12}H$	$(CN)_{12}$	241	–	–
$CB_{11}(CF_3)_{12}H$	$(CF_3)_{12}\rightarrow(CF_3)_7$	197	–	–
$CB_{11}(SO_2CF_3)_{12}H$	$Tf_{12}\rightarrow Tf_7$[f]	255	–	–

[a] The site of protonation of the most stable protonated form of each acid. See footnote to Table 3 for explanations. [b] Values at 298 K, given in kcal/mol (1 cal = 4.184 J). [c] Protonated on the boron B12. B12 bears two symmetrically arranged hydrogens (see also Figure 2a). [d] F_{12} with 3-21G*. [e] $F_{12}\rightarrow F_7$ with 3-21G*. [f] Tf denotes SO_2CF_3 group; the proton is attached to an oxygen atom and gives H-bond to another oxygen atom.

much weaker acidities than the corresponding Brønsted−Lewis complex acids (pyrosulfuric and polysulfuric acids, polyphosphoric acid, $HAlCl_4$, $HAlBr_4$, HBF_4, HPF_6, pyrofluorosulfuric acid and its higher homologues, FSO_3SbF_5H, hexafluoroantimonic acid, etc.). In some cases the latter compounds and the polycyanated relatively simple hydrocarbons such as cyanoform, pentacyanocyclopentadiene, pentacyanopropene, etc. are calculated to be stronger acids than the classical mineral acids such as sulfuric acid by up to 50 kcal/mol (by 37 pK_a units!).

The calculated[32] DFT/DNP gas-phase deprotonation energies (at 0 K but including ZPVE) and ΔH_{acid}(298 K) calculated using DFT B3LYP 6-311+G** are in a reasonable agreement, within 2−3 kcal/mol.

Conjugate Brønsted−Lewis Superacids. The acidity order $FSO_3SbF_5H > HSbF_6 > HAlCl_4 \approx HAlBr_4 > HTaF_6 > HPF_6 > HBF_4$ for the group of classical conjugate Brønsted−Lewis superacids is calculated in the present work using the DFT B3LYP//6-311+G** approach. For the compounds that are comparable, the results qualitatively agree with the recent findings[32] using somewhat lower levels of theory and basis sets. Although generally not treated as such, sulfonic (and also carboxylic) acids can also be regarded as Brønsted−Lewis conjugate superacids, whereby the Lewis component is SO_3 (CO_2 in the case of carboxylic acids) and the Brønsted component is H_2O, HF, CF_3H, etc.

Scheme 1 summarizes the calculated increases of the intrinsic acidity that accompany the formation of these conjugate Brønsted−Lewis superacids.

These changes in the intrinsic acidity of the parent Brønsted acid are in the same range as in the case of complex formation of SO_3 with HF, H_2O, CH_4, and CF_3H. In the case of the formation of hexafluoroantimonic acid, $HSbF_6$, the acidity change reaches more than 100 kcal/mol. At the same time hexafluoroantimonic acid is calculated to be in the gas phase only by 2 kcal/mol stronger acid than $HAlCl_4$ which, in its turn, is significantly stronger than HBF_4, HPF_6, and $HTaF_6$ but practically equal to tetrabromoaluminic acid $HAlBr_4$.

The calculated gas-phase acidity of the main component of Magic Acid—FSO_3SbF_5H—is rather close to that of hexafluoroantimonic acid: the difference of 5.1 kcal/mol is predicted. PM3 calculations performed in this work show that the substitution of even five F atoms for OSO_2F or CN groups does not increase the acidity of the resulting acid by more than 10 kcal/mol.

It can be seen from Table 2 and Scheme 1 that formation of conjugate Brønsted−Lewis superacids via the interaction of H_2O with SO_3 or HF with SO_3 and further of SO_3 with sulfuric acid and its derivatives is also accompanied by a very significant increase of their intrinsic acidity. Thus, the transfer from H_2O to H_2SO_4 results in a very sharp 82 kcal/mol increase of the acidity of the parent molecule. Further interaction of SO_3 with H_2SO_4 to form $H_2S_2O_7$ results in a 27 kcal/mol increase of the acidity, whereas further transfer to $H_2S_3O_{10}$ increases the acidity by 13.2 kcal/mol. Similar transfer from HF to FSO_3H is accompanied by the increase of the acidity by 71.1 kcal/mol, whereas the transfer from FSO_3H to $F(SO_3)_2H$ increases in the acidity by 21.8 kcal/mol and a further transfer to $H(SO_3)_3F$ and $H(SO_3)_4F$ still by 11.9 and 7.9 kcal/mol, respectively. The transfer from water to orthophosphoric acid (H_3PO_4) increases the acidity by 65.2 kcal/mol, whereas the transfer from the latter to pyrophosphoric acid results in an increase by 21.7 kcal/mol of the calculated intrinsic acidity which is quite comparable with the acidity increases in case of transfers from H_2SO_4 or its analogues to their conjugate Brønsted−Lewis acids with SO_3.

The extrapolation of the calculated acidity data for pyrosulfuric acid $HO(SO_3)_nH$ and fluoropyrosulfuric acid $F(SO_3)_nH$ families to $n = \infty$ should give at the infinitely long chain for both series the same limiting values of $(\Delta G_{acid})_{limit}$. This extrapolation is difficult to carry out using the present data, because the "plateau" has not been reached yet. A rather rough estimate of $(\Delta G_{acid})_{limit}$ would be around 240 kcal/mol.

In a similar way, the formal transfer from CH_4 to methanesulfonic acid increases the acidity of the former species by 95 kcal/mol. The transfers from CF_3H to trifluoromethanesulfonic acid and from the latter to $CF_3(SO_3)_2OH$ are predicted to result, respectively, in 72.4 and 21 kcal/mol increases of the intrinsic acidity of the resulting species (see also Figure 1). In agreement with some solution chemistry results[1] (but in disagreement with others[60]) and in contrast with the gas-phase studies and G2-(MP2) calculations, fluorosulfonic acid is predicted to be moderately stronger than trifluoromethanesulfonic acid at DFT B3LYP 6-311+G** level of theory (vide supra). The same order is maintained also for their corresponding conjugate Brønsted−Lewis acids with SO_3 where $F(SO_3)_2H$ is calculated to be by 2.7 kcal/mol stronger acid than $CF_3(SO_3)_2H$.

CH and NH acids. It was experimentally demonstrated[25] that several CH and NH acids can surpass by their gas-phase acidity their OH and SH counterparts. The present calculations confirm those findings. They show that the acidity of the representatives of those classes of compounds, especially that of polycyanated alkenes, $HC(CN)_2C(CN){=}C(CN)_2$ and $C_5H(CN)_5$ (pentacyanocyclopentadiene), can reach or even exceed the acidity of the strongest representatives of the conjugate Brønsted−Lewis superacids.

Pentacyanocyclopentadiene, the compound first made by O. Webster in 1966,[34] is calculated to be equal or to exceed by its intrinsic acidity ($(\Delta G_{acid})_{calc}$ = 250.1 kcal/mol) even FSO_3SbF_5H, $HSbF_6$, $F(SO_3)_3H$, $HAlCl_4$ and other extremely strong superacids. The consecutive introduction of five cyano groups into the cyclopentadiene (ΔG_{acid} = 347.7 kcal/mol)[29] leads to ~100 kcal/mol increase in its intrinsic acidity due to extra stabilization by resonance and polar effects of the planar and highly symmetrical (point group D_{5h}) $C_5(CN)_5^-$ moiety.

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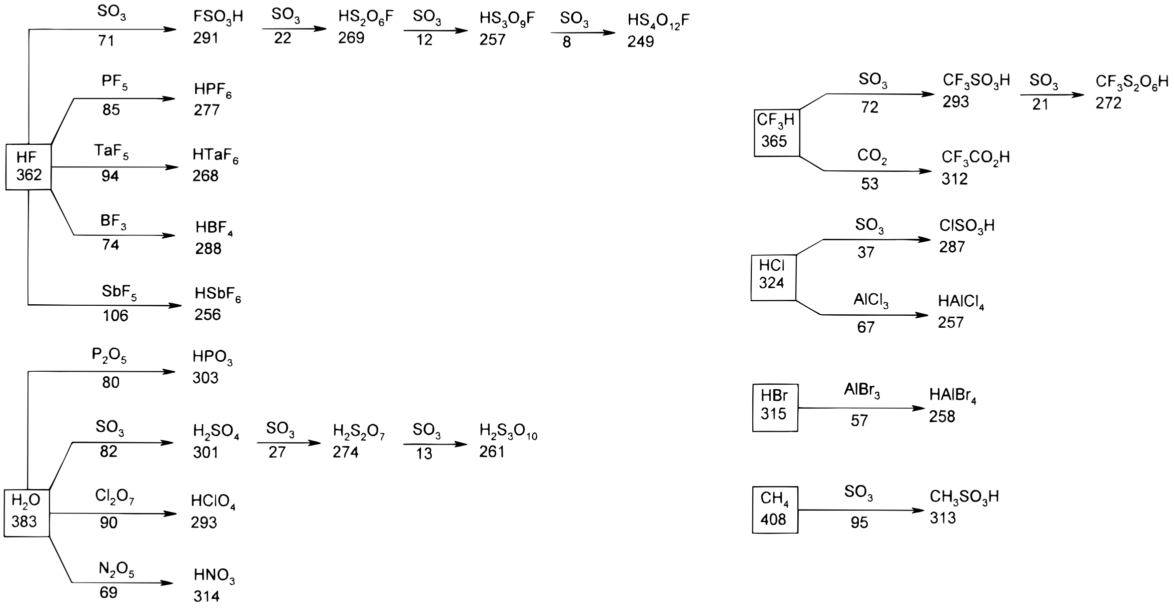
(60) Fujinaga, T.; Sakamoto, I. *J. Electroanal. Chem.* **1977,** *85*, 185−201.

Scheme 1. Calculated (DFT B3LYP 6-311+G**) Gas-Phase Acidity Increase of Several Brønsted Acids upon Complex Formation with Lewis Acids



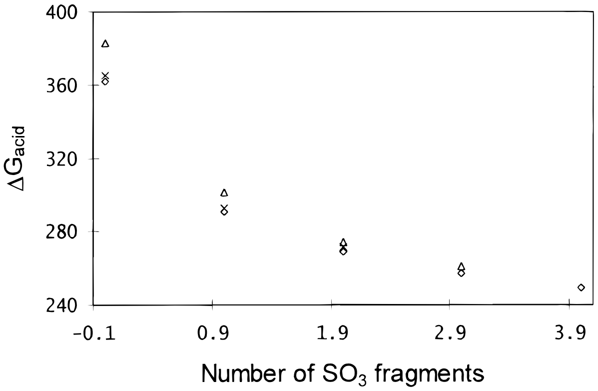


Figure 1. Increase of the acidity of H_2O (△), CF_3H (×), and HF (◇) upon consecutive introduction of SO_3 fragments.

It is also interesting to note that the calculated acidity order for the trisubstituted methanes considered in this work is $CF_3SO_2C(CN)_2H > HC(CN)_3 > HC(SO_2F)_3 > HC(NO_2)_3$. This is not surprising because the calculations show that in the first two cases the planarity of the anionic center is being observed, whereas in the case of trinitromethane and trisfluorosulfurylmethane the nonplanarity of the center causes nonadditivity effects which lead to the significantly reduced acidity (see also ref 25).

This conclusion is supported by the fact that the fractional additivity factor[25] for the transfer from CH_4 to $HC(CN)_3$ is 0.86, whereas for the analogous transfer to $CF_3SO_2CH(CN)_2$ it is 0.80, to trinitromethane, 0.65, and to $HC(SO_2F)_3$, 0.57.

In accordance with the earlier experimental findings for $CH_2(SO_2CF_3)_2$ and $HN(SO_2CF_3)_2$,[25] bisfluorosulfurylimide is a stronger acid than its corresponding CH counterpart, $CH_2(SO_2F)_2$. The similar order of acidities holds also for monotriflyl-substituted methane and ammonia and maintains roughly the experimentally observed acidity gap between ammonia and methane ($\Delta\Delta G_{acid} = 10.5$ kcal/mol)[29] in accordance with the classical considerations about the higher acidity of the NH acidity center as compared with the similarly substituted CH acidity site.

Cluster-Fragments of the Active Acidic Sites of Zeolites. The acidity of the following compounds that model the elementary fragments of zeolites was calculated by using DFT B3LYP//6-311+G** approach:

$[H_3Al{-}O{-}SiH_3]^-\ H^+$ (**H1**); $[(HO)_3Al{-}O{-}Si(OH)_3]^-\ H^+$ (**OH1**); $[F_3Al{-}O{-}SiF_3]^-\ H^+$ (**F1**); $[H_2Al(OSiH_3)]^-\ H^+$ (**H2**); $[H_3Al{-}O{-}H_2Si{-}O{-}AlH_2{-}O{-}SiH_3]^{2-}\ 2H^+$ (**2H2**). One can see from Table 2 that the acidities of the simplest possible fragments **H1** and **OH1** are practically equal: 297.8 and 298.0 kcal/mol, respectively. At the same time, both of them already surpass the calculated Brønsted acidity of such mineral acids as H_2SO_4, HPO_3, HNO_3. Replacement of all hydrogen atoms in **H1** by fluorine atoms increases the intrinsic acidity, as compared to **H1**, by as much as 40 kcal/mol. The calculations show that upon transferring from **H1** to more complicated clusters, e.g., **H2** ($(\Delta G_{acid})_{calc} = 293.6$ kcal/mol) or **2H2** ($(\Delta G_{acid})_{calc} = 290.0$ kcal/mol) the intrinsic Brønsted acidity of the fragment is expected to increase correspondingly by 4.2 and 7.8 kcal/mol.

Performance of DFT B3LYP 6-311+G Calculations.** Similar to the evaluation of the performance of G2(MP2) theory, for the compounds listed in Table 2 the comparisons with the experimental data are available only for 8 acids. In this case the differences between experimental and calculated values are somewhat more pronounced than in the case of G2 or G2(MP2) theory. Thus, for HPO_3 the difference is 0.1 kcal/mol, for CF_3COOH, 4.6 kcal/mol, for HNO_3, 3.8 kcal/mol, for H_2SO_4, 1.0 kcal/mol, for FSO_3H, 9.2 kcal/mol, for CF_3SO_3H, 7.0 kcal/mol, for CF_3COSH, 4.3 kcal/mol, and for CH_3SO_3H, 2.3 kcal/mol. At the same time DFT B3LYP calculations at the 6-311+G** level give results that are closer to the experimental ones (mostly deprotonation energies could be compared) than in the case of DFT/DNP approach[32] which uses virtually the 6-31G** basis set.

The performance of several levels of DFT theory in reproducing of the experimental acidity values for 35 different simple Brønsted acids was recently evaluated by Merrill and Kass.[54] From this work it is evident that in general cases only the approximate linear relationships of the type $PA_{expt} = \alpha PA_{calc} + \beta$ will be found where α and β are coefficients, whereas $\alpha \neq 1$ and $\beta \neq 0$. However, B3LYP approach with 6-311+G** basis set was not involved in that study, but determination of the regression coefficients of the corresponding linear scaling equation for the present DFT B3LYP/6-311+G** calculations was undertaken in another work of the present authors.[59]

The comparison of $(\Delta G_{\mathrm{acid}})_{\mathrm{calc}}$ values with their experimentally available counterparts was done for 53 relatively simple Brønsted acids which represent different classes of compounds of highly variable (~100 kcal/mol) acid strength.

The statistical analysis of those data at B3LYP/6-311+G** level leads to the correlation equation $(\Delta G_{\mathrm{acid}})_{\mathrm{calc}} = (-19.5 \pm 4.7) + (1.048 \pm 0.013)\,(\Delta G_{\mathrm{acid}})_{\mathrm{exp}}$ ($r^2 = 0.992$, $s = 2.8$). The DFT B3LYP//6-311+G** approach progressively overestimates the acidity of the most acidic molecules ($\Delta G_{\mathrm{acid}} \leq 340$ kcal/mol) and underestimates the acidity of the weakest acids ($\Delta G_{\mathrm{acid}} \geq 400$ kcal/mol), whereas the acidity of the moderately acidic compounds ($340 \leq \Delta G_{\mathrm{acid}} \leq 400$) is reproduced with the smallest error.

The above equation was used for calculation of the scaled “experimental” values $(\Delta G_{\mathrm{acid}})_{\mathrm{scaled}}$ of the intrinsic Brønsted acidities of the strong acids listed in Table 2. These $(\Delta G_{\mathrm{acid}})_{\mathrm{scaled}}$ values are given in the last column of this table. The scaled values of DFT B3LYP 6-311+G** acidities are in satisfactory agreement with the available respective quantities from the higher level G2(MP2) calculations (cf. Tables 1 and 2). Therefore, both quantities should be used in practice as the best substitutes for the so far unavailable experimental values of intrinsic acidities of different Brønsted superacids listed in Table 2.

Conjugate Acids of Monocarborane Anion $CB_{11}H_{12}^-$ and Its Substituted Derivatives. The calculated acidity of the conjugate Brønsted acid (see Figure 2a) of unsubstituted monocarborane anion $CB_{11}H_{12}^-$ at DFT B3LYP calculations at 6-311+G** level is 265.5 kcal/mol (260.4 kcal/mol using 6-31+G* basis set). This means that in the intrinsic acidity row this superacid is expected to surpass all classical strong Brønsted acids, except pentacyanocyclopentadiene, FSO_3SbF_5H, $HSbF_6$, $F(SO_3)_4H$, $F(SO_3)_3H$, **F1**, $HAlCl_4$, $HAlBr_4$, and $H_2S_3O_{10}$. The successive fluorination of the species increases the acidity significantly: the predicted intrinsic gas-phase acidity 12-F−$CB_{11}H_{11}H$ is 251.9 kcal/mol, that of 7,8,9,10,11,12-$CB_{11}H_6F_6H$ is 231.0 kcal/mol, whereas the acidity of the dodecafluorosubstituted derivative $CB_{11}F_{12}H$ (Figure 2b) is calculated to be still much higher: 209.2 kcal/mol (see Table 3). In other words, the intrinsic basicity of the superweak anionic base, $CB_{11}F_{12}^-$ is expected to be in the same range as for example those for the following neutral bases: 1,4-phenylenediamine ($\Delta G_{\mathrm{base}} = 208.9$ kcal/mol),[61] 1-naphthylamine ($\Delta G_{\mathrm{base}} = 209.2$ kcal/mol),[61] and *N*,*N*-dimethylacetamide ($\Delta G_{\mathrm{base}} = 209.6$ kcal/mol).[61] This means, that $CB_{11}F_{12}H$ should be considered the strongest neutral Brønsted superacid which exceeds sulfuric acid by its calculated acidity by 90 kcal/mol and pentacyanocyclopentadiene by 41 kcal/mol (vide supra). Such high Brønsted acidity of this species is due to the enormous stability of its icosahedral conjugate anion $CB_{11}F_{12}^-$ which is due to its high symmetry, the lack of lone pairs and π-electrons, tangentially delocalized σ-bonding, and large size (~1 nm) of the anion. The combined action of these factors makes the binding of the proton to the potential protonation sites of the internally highly stabilized anion very unfavorable.

The results of semiempirical PM3 calculations and lower level (3-21G*) ab initio calculations (see Table 4) indicate, that several additional superacidic conjugate acids of the derivatives of the monocarborane anion $CB_{11}H_{12}^-$ are expected to have acidities comparable to those of conjugate acids of $CB_{11}H_6F_6^-$ and $CB_{11}F_{12}^-$. In the case of the dodecatrifluoromethyl derivative, $CB_{11}(CF_3)_{12}^-$, the results of PM3 calculations ($\Delta H_{\mathrm{acid}} = 197$ kcal/mol) indicate that the challenge of reaching a landmark deprotonation energy level 200 kcal/mol for neutral Brønsted superacids—conjugate acids of the least coordinating and least basic anions—is reached.

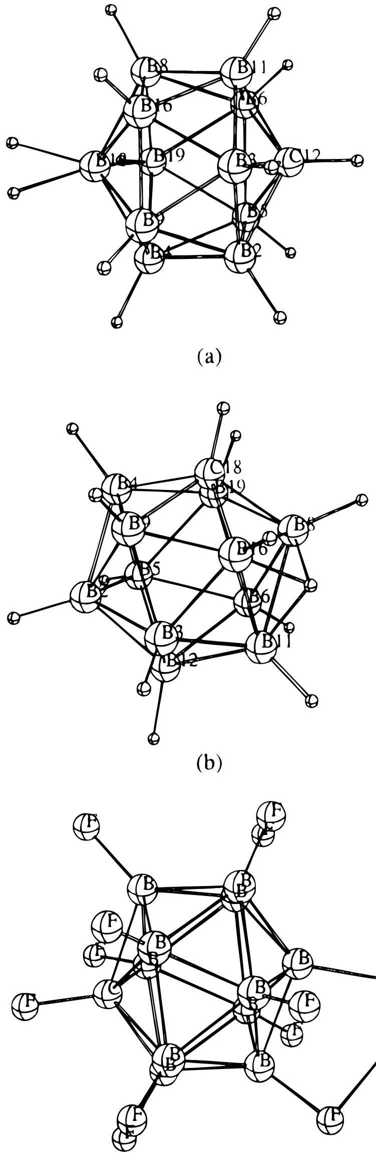


Figure 2. Optimized structures of protonated forms of some monocarboranes and their fluorinated derivatives. (a) $CB_{11}H_{12}H$, B3LYP calculations at 6-311+G** level. (b) $CB_{11}H_{12}H$, protonation on facet 7−8−12, B3LYP calculations at 6-31+G* level. (c) $CB_{11}F_{12}H$, B3LYP calculations at 6-31+G* level.

The site of protonation is a special question with the carborane anions. There are no data available in the literature concerning the attachment of proton to these species, but studies have been carried out on the geometry of the complexes of $CB_{11}H_{12}^-$ and its derivatives with metal ions (see ref 44 and references therein). Those studies show, that the hydrogen (or some heteroatom in the case of substituted carboranes) attached to the boron atom in the 12 position (antipodal to the unique carbon atom), is always involved in metal−$CB_{11}H_{12}^-$ bonding. Assuming some analogy between the behavior of $CB_{11}H_{12}^-$ toward metal ions and the proton, it is reasonable to expect that the most favorable site of protonation would also be the H12 (or X12 in the case of substituted carboranes). However, because of the very small size of the proton compared to that of the metal ions, two

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[61] Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

additional possibilities should be considered when looking for the most favorable protonation site. First, the proton can also be attached on the "surface" of the carborane skeleton, between the hydrogens (or substituents). Second, proton can be placed *inside* the carborane cage.

Various protonation sites were considered for the parent anion $CB_{11}H_{12}^-$ using DFT B3LYP approach at 6-31+G* level. The results, in accordance with the results of DFT B3LYP/6-311+G** calculations (vide supra, Figure 2a) show that in the case of this anion the most favorable site of protonation is the boron atom in the 12 position. Stable structures are also obtained, when the proton is placed on the surface of the carborane cage in the middle of a "facet" formed by three atoms (see Figure 2b). Structures with the proton on the "edge" of the icosahedron did not prove stable (the proton drifted to a facet during the optimization procedure or imaginary vibration detected as a result of the frequency calculation). Due to the symmetry of the anion, there are four different facet-protonated forms that are possible, and three of them were found to be stable (see Table 3). The structure with the proton in the middle of the triangle 1−2−3 did not prove to be stable—the proton drifted to the center of the 2−3−7 triangle. Also, the structure of the protonated species with the proton inside the carborane cage did not prove to be stable. In the course of the geometry optimization the proton moved out of the cage and resided on the "surface" of the boron framework.

Various protonation sites of the derivatives of $CB_{11}H_{12}^-$ were investigated at PM3 and HF 3-21G* levels of theory. The most favorable sites of protonation were found to be the substituent in the position 12 and the surface of the cage between the positions 7, 8, and 12. For monofluoro-, hexafluoro-, and dodecafluoroderivatives these two possibilities were calculated also using the DFT B3LYP 6-31+G* method. For the monofluoroderivative the surface-protonated form was found to be more favorable by $\Delta\Delta G_{\mathrm{acid}} = 10.4$ kcal/mol, for the hexafluoroderivative the surface-protonated form proved to be by $\Delta\Delta G_{\mathrm{acid}} = 4.2$ kcal/mol lower in energy, and for the dodecafluoroderivative the surface-protonated form is less stable by $\Delta\Delta G_{\mathrm{acid}} = 0.7$ kcal/mol. With the two polyfluorinated derivatives, the F-protonated form has somewhat bidentate character, that is, the proton is attached to one of the F atoms and simultaneously forms H-bond with the neighboring one (see Figure 2c). The lack of this additional stabilization by hydrogen bond in the case of the monofluorinated carborane anion together with the higher electron density of the boron framework (as compared to the polyfluorinated species) is probably the reason why in the case of this ion the F-protonated form is significantly less stable than the surface-protonated form. The bidentate character of the substituent-protonated forms was also found for most of the other substituted carboranes that were calculated at PM3 and 3-21G* levels.

When acidities approach 200 kcal/mol, the principles of the design of superstrong[25,62] acids have to be somewhat reconsidered: the idea of progressive introduction of highly electronegative, correctly oriented polarizable dipolar electron-accepting substituents into the acidity site is no longer very fruitful. By using this approach, it is possible to enhance the acidity of a particular acidity center. However, with acidities as high as those encountered with the carborane acids, new, more favorable sites of protonation tend to emerge in the periphery of the molecule, at these same substituents, which are used to enhance the acidity of that particular acidity site. Thus, instead of designing the acid, one should rather design the anion. One should take care not to introduce into the anion any features that could attract the proton—loosely bound electron pairs and loosely bound π-electrons. Simultaneously, the anion should be large and with a charge as delocalized as possible. These principles are well-illustrated by the acidity order (PM3 level) of the dodeca-substituted carborane acids: $CF_3 > F > CN > Cl > CF_3SO_2 > H$. In particular the relatively poor "performance" of the CF_3SO_2 substituent is very characteristic in this context.

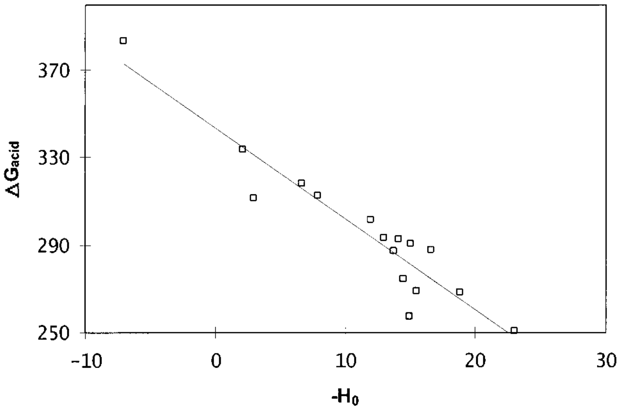

Figure 3. Correlation between the calculated intrinsic acidities of some superacids and their corresponding Hammett acidity function H_0 values.

Intrinsic Acidity of Superacids versus Acidity of the Neat Acids. There is a rather approximate correlation between the calculated intrinsic acidities (at DFT B3LYP 6-311+G** level) of some superacids and their corresponding Hammett acidity function H_0 values for the neat acids, as can be seen from Figure 3. The H_0 values are those given in the Introduction. The points for HCOOH ($H_0 = -2.2$),[63] CF_3COOH ($H_0 = -3$),[63] H_3PO_4 ($H_0 = -6.7$),[64] CH_3SO_3H ($H_0 = -7.9$),[65] and water ($H_0 \equiv$ pH $= 7$) as a natural reference state for aqueous solutions of strong mineral acids where H_0 becomes identical to pH were also included. For most systems (H_2O, HCOOH, H_2SO_4, CF_3COOH, HF, CH_3SO_3H, CF_3SO_3H, FSO_3H, H_3PO_4, $ClSO_3H$, $HClO_4$) the H_0 value corresponds to the pure (100%) acid. For $H_2S_2O_7$ and $HSbF_6$ the used value corresponds to 50 mol % mixture of components, the H_0 value for FS_2O_6H corresponds to 4 mol % of SO_3 in the mixture, for $HTaF_6$ to 0.6% solution of TaF_5 in HF, for HBF_4 to 7 mol % of BF_3 in HF, and for $HAlCl_4$ to a molten mixture of 55% $AlCl_3$ in 1-ethyl-3-methyl-1*H*-imidazolium chloride where HCl was dissolved at the partial pressure of 1 atm. For the Magic Acid the value $H_0 = -23^1$ corresponding to the 1:1 mixture was used.

If the correlation analysis includes the collection of points for all of the acids except HF and $HSbF_6$, then the following approximate linear relationship between the calculated intrinsic acidities of strong acids and the H_0 functions of their neat solutions holds:

$$\Delta G_{\mathrm{acid}} = (343.6 \pm 5.2) + (4.16 \pm 0.38)\, H_0 \qquad (2)$$

$$r^2 = 0.894 \quad s = 10.9 \quad n = 16$$

This relationship covers the H_0 range of 30 units and ΔG_{acid} range of 132 kcal/mol. The points for HF and $HSbF_6$ deviate (toward lower H_0 values and higher ΔG_{acid} values) significantly

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from this relationship: 16 units of H_0 and 68 kcal/mol on the ΔG_{acid} scale for HF and 9 units of H_0 and 36 kcal/mol on ΔG_{acid} scale for $HSbF_6$.

In the liquid state the molecules of HF are known to form different aggregates for example, dimers $(HF)_2$, trimers $(HF)_3$, etc.[62,66] The acidic dissociation of these is heavily favored due to the formation of exceptionally strongly H-bond-stabilized anions, for example, FHF^-, according to the scheme:

$$(HF)_2 \rightleftarrows H^+ + FHF^- \tag{3}$$

DFT B3LYP calculations at 6-311+G** basis set show, that the intrinsic acidity of the dimer of HF is 319 kcal/mol, that is, by ~40 kcal/mol higher than the same quantity for the monomeric species. The use of the ΔG_{acid} value of the dimeric HF instead of that of the monomeric HF in the correlation analysis moves the point of HF practically to the common line with the other acids on the ΔG_{acid} vs H_0 plot and evidences about the very significant role of the dimeric form of HF in determining the acidity of its neat solution.

The higher than expected from the simple formula liquid-phase acidity of $HSbF_6$ can, in principle, be accounted for by the presence in neat hexafluoroantimonic acid of the higher aggregates, for example, HSb_2F_{11}, etc. whose intrinsic acidity is expected to be higher than that of $HSbF_6$.

The majority of the H_0 values (H_2SO_4, CF_3COOH, CF_3SO_3H, FSO_3H, HBF_4, $ClSO_3H$, $HClO_4$, $HAlCl_4$, etc.) group in the range of $-16 \leq H_0 \leq -12$, whereas their intrinsic gas-phase acidities vary by at least 40 powers of 10. The H_0 acidity function for hexafluoroantimonic acid and hexafluorotantalic acid are significantly different from that range (−30 and −26, respectively). Evidently, the strong leveling of the acidity of those superacids takes place in their neat solutions, especially for the hydroxylic acids.

The slope of eq 2 shows that the substituent effects on the intrinsic acidity of Brønsted superacids are attenuated by solvent effects 3.0 ± 0.3 times (on logarithmic scale) while going from the gas phase into solution. Comparable or somewhat lower solvent attenuation factors have been found for the transfer of several acid−base equilibria from the gas phase into aqueous solution or DMSO.[67−70]

Feasibility of the Spontaneous Proton-Transfer Equilibria between Neutral Brønsted Acid and Neutral Brønsted Base. The currently existing gas-phase scale of Brønsted acidities of neutral acids spans from methane ($\Delta G_{acid} = 407.5$ kcal/mol) to $(n\text{-}C_4F_9SO_2)_2NH$ ($\Delta G_{acid} = 284.1$ kcal/mol). The presently reported calculations of gas-phase acidities of neutral Brønsted superacids predict the expansion of this scale well into the territory of the of the weakest organic cationic Brønsted acids, that is, into the range of basicities of the strongest neutral organic bases. At the same time the continuous intrinsic basicity scale of the neutral Brønsted bases covers the range from $\Delta G_{base} = 41$ kcal/mol for helium to $\Delta G_{base} = 248.4$ kcal/mol.[61,71] The somewhat outdistanced region of very high basicity from $\Delta G_{base} = 249.7$ kcal/mol (NaOH) to 337.5 kcal/mol (Cs_2O) enters into and overlaps with the area covered by ΔG_{acid} values for strong and superstrong acids and is so far represented with experimentally determined values for such superbases as alkali metal hydroxides, alkali metal oxides and oxides of alkali earth metals.[61]

It was recently shown[72] via DFT B3LYP calculations at 6-311+G** level that the basicity range between 250 and 300 kcal/mol is predicted to be covered using derivatives of organic superbases—phosphorus imines (phosphazenes) and phosphorus ylides (phosphoranes) and nitrogen ylides. So, the ΔG_{base} value for $(H_2N)_3P{=}N{-}P({=}NH)(NH_2)_2$ is predicted to be 263 kcal/mol, for $(H_2N)_3P{=}N{-}P({=}CH_2)(NH_2)_2$, 277 kcal/mol, and for $(H_2N)_3N{=}CH_2$, 279 kcal/mol. Even higher basicity estimates—up to a PA value 335 kcal/mol—of superstrong quinodiimine bases have been given.[73]

With the findings of the present work the overlap-area for the basicities of neutral and anionic bases (acidities of neutral and cationic Brønsted acids) covers the range of ~100 kcal/mol (from 209 kcal/mol for $CB_{11}F_{12}H$ to 337 kcal/mol for Cs_2O). Therefore, the realization of the spontaneous gas-phase proton-transfer equilibria between neutral Brønsted acids HA_i and neutral Brønsted bases B_j with similar or overlapping values of gas-phase acidity and gas-phase basicity, respectively, according to eq 4 has been for some time a problem, which is waiting for

$$B_j + HA_i \rightleftarrows B_jH^+\cdots A_i^- \rightleftarrows B_jH^+ + A_i^- \tag{4}$$

a practical realization rather than a complicated theoretical solution. Some possible ways of its realization have been proposed recently.[74]

If the proton-transfer equilibrium 4 leads to the ion pair $B_jH^+\cdots A_i^-$ as the product, then its energetic realization will be much more favorable by the rather significant Coulombic stabilization due to electrostatic interactions of its anionic and cationic counterparts A_i^- and B_jH^+. The latter point is illustrated by simple 3-21G* calculations of interactions of acid−base pair consisting of K_2O and perchloric acid.[75] The sum of the total energies of free ions ClO_4^- and K_2OH^+ is by 57.2 kcal/mol more negative (favorable) than the same for the neutral molecules. However, the ion-pair-like interaction product $K_2OH^+\cdots ClO_4^-$ is in its turn by 128 kcal/mol energetically more favorable than the pair of infinitely distanced electrostatically noninteracting ions K_2OH^+ and ClO_4^-.

Conclusions

1. For the first time G2 and G2(MP2) calculations have been performed to calculate the acidity and deprotonation enthalpy of classical strong mineral acids $HClO_4$, FSO_3H, CF_3SO_3H, H_2SO_4, HBF_4, HPO_3, and HNO_3. The acidity of these species is found to be decreasing in the indicated succession. Also, the intrinsic acidities and gas-phase deprotonation enthalpies were calculated by using the density functional theory approach with B3LYP hybrid functional with 6-311+G** basis set for 39 neutral strong or superstrong Brønsted acids, Brønsted−Lewis conjugate acids, and some compounds modeling the acidic clusters of zeolites. The DFT method overestimates the acidity of superacidic and strongly acidic compounds ($\Delta G_{acid} \leq 340$

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kcal/mol) and underestimates the acidity of the weakest acids ($\Delta G_{\mathrm{acid}} \geq 380$ kcal/mol). In the range of moderately acidic compounds ($340 \leq \Delta G_{\mathrm{acid}} \leq 380$ kcal/mol) this method yields rather good or satisfactory agreement with the experimentally measured values. As expected, G2 and G2(MP2) theories describe the acidities of different compounds better than DFT B3LYP//6-311+G**. However, the DFT results could also be used for the estimation of the acidity of compounds that are out of reach of G2 and G2(MP2) theory.

2. In the case of practically all considered families of compounds extremely high acidities (low ΔG_{acid} values) could be reached. If the compounds were started from HF as the parent acid, then the estimated ΔG_{acid} as low as 249.0 kcal/mol (for $F(OSO_2)_4H$) could be reached by formation of Brønsted−Lewis conjugate acids by consecutive complexation with SO_3 molecules. Also, a very low ΔG_{acid} value ($\Delta G_{\mathrm{acid}}(HSbF_6) = 255.5$) could be reached by complexation of HF with SbF_5.

Intrinsic acidities at least as high as those of the strongest Brønsted−Lewis superacids could be reached in the case of progressive introduction of highly electronegative, correctly oriented polarizable dipolar electron-accepting substituents into the acidity site. Indeed, the introduction of five CN groups into cyclopentadiene is expected to lead to the acidity $\Delta G_{\mathrm{acid}} = 250.1$ kcal/mol which is lower than the corresponding quantity even for hexafluoroantimonic acid ($\Delta G_{\mathrm{acid}} = 255.5$ kcal/mol). However, by far the highest intrinsic Brønsted acidity ($\Delta G_{\mathrm{acid}} = 209$ kcal/mol) for dodecafluorosubstituted carborane acid $CB_{11}F_{12}H$ is predicted to exceed the intrinsic acidity of sulfuric acid by about 90 kcal/mol or by almost 70 powers of 10, whereas semiempirical PM3 calculations suggest that conjugate acid of the dodecatrifluoromethylmonocarborane $CB_{11}(CF_3)_{12}^-$ could be the first neutral Brønsted superacid whose acidity (deprotonation energy) is expected to be below the landmark 200 kcal/mol level.

3. An approximate linear relationship between the calculated intrinsic acidities of some superacids or their principal components and the corresponding Hammett acidity function H_0 of the respective neat acids was found to hold.

4. The simultaneous existence of the widely overlapping areas on the gas-phase acidity scale of neutral and cationic Brønsted acids is strong evidence for the feasibility of the spontaneous proton-transfer equilibria between neutral Brønsted acids and bases.

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