

The Strongest Acid

The Strongest Brønsted Acid: Protonation of Alkanes by H(CHB₁₁F₁₁) at Room Temperature**

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Abstract: What is the strongest acid? Can a simple Brønsted acid be prepared that can protonate an alkane at room temperature? Can that acid be free of the complicating effects of added Lewis acids that are typical of common, difficult-to-handle superacid mixtures? The carborane superacid H(CHB₁₁F₁₁) is that acid. It is an extremely moisture-sensitive solid, prepared by treatment of anhydrous HCl with [Et₃Si–H–SiEt₃][CHB₁₁F₁₁]. It adds H₂O to form [H₃O][CHB₁₁F₁₁] and benzene to form the benzenium ion salt [C₆H₇][CHB₁₁F₁₁]. It reacts with butane to form a crystalline tBu⁺ salt and with n-hexane to form an isolable hexyl carbocation salt. Carbocations, which are thus no longer transient intermediates, react with NaH either by hydride addition to re-form an alkane or by deprotonation to form an alkene and H₂. By protonating alkanes at room temperature, the reactivity of H(CHB₁₁F₁₁) opens up new opportunities for the easier study of acid-catalyzed hydrocarbon reforming.

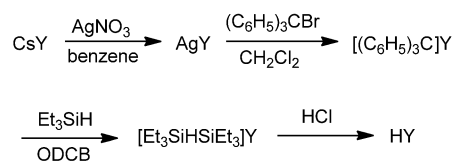
For the past decade, the strongest acid to be isolated and fully characterized has been the chlorinated carborane acid, H(CHB₁₁Cl₁₁).^[1,2] More recently, this has been equaled by the comparably strong, isoelectronic, all-boron diprotic superacid, H₂(B₁₂Cl₁₂).^[3] The superior strength of these Brønsted acids has been established in all phases. In solution, the fact that both readily protonate benzene (whereas oxyacids do not) places them ahead of HFSO₃, the previous strongest pure acid measured on the H₀ scale.^[4] In the gas phase, the calculated^[5] and measured^[6] deprotonation enthalpy of H(CHB₁₁Cl₁₁) is the lowest of any available acid. The νNH anion basicity scale^[7] indicates that carborane anions are less basic than the oxyanions of traditional acids. This same scale indicates that fluorinated carborane anions are less basic than chlorinated carborane anions, so the conjugate acid H(CHB₁₁F₁₁) should be a stronger acid than H(CHB₁₁Cl₁₁).

Calculated gas-phase deprotonation energies concur.^[5] There is, of course, no guarantee that weaker anion basicity leads to an isolable stronger conjugate acid. The anion must also be chemically stable to H⁺.^[8] However, the stability of fluorinated carborane anions^[9] towards the potent Lewis acidity of trialkylsilylium ions^[10] augurs well for their stability towards H⁺.

Indeed, there was a preliminary report in 2007 of two fluorinated carborane acids, H(HCB₁₁F₁₁) and H(EtCB₁₁F₁₁).^[10] As evidence of formulation, an IR spectrum of the latter was given. By analogy to H(CHB₁₁Cl₁₁), which is known from X-ray analysis to have a linear polymeric structure with H⁺ bridges between anion Cl atoms, and from IR spectroscopy to have low-barrier H-bonding,^[11] the expected IR features for H(EtCB₁₁F₁₁) were present. These include two bands at about 1705 and 1620 cm^{−1} as candidates for νFHF and a band at about 920 cm^{−1} for δFHF, along with expected νBB and νBF bands from the anion at circa 1300 and 700 cm^{−1}, respectively.

Given that there has been no follow-up to this preliminary report in the intervening six years, we were curious whether we could reproduce this work and prepare a fluorinated carborane acid in synthetic amounts for reactivity studies with hydrocarbons. We chose the non-alkylated anion CHB₁₁F₁₁[−] for our studies, based on concern for the chemical stability of the ethyl group in EtCB₁₁F₁₁[−]. From preliminary investigations into the reactivity of the chlorinated carborane acid H(CHB₁₁Cl₁₁) with alkanes at somewhat elevated temperatures, we had reason to believe that fluorinated carborane acids might react with alkanes at room temperature, thus giving H(EtCB₁₁F₁₁) the capability of reacting with its own ethyl group. An indication that this may be occurring is suggested by the IR spectrum reported for H(EtCB₁₁F₁₁)^[10] where two of the three νCH bands of the ethyl group in the 2900–3020 cm^{−1} region are nearly absent in comparison to other EtCB₁₁F₁₁[−] salts (see Figure S8 in the Supporting Information of Ref. [10]).

The synthesis of H(CHB₁₁F₁₁) (Scheme 1) was eventually achieved using much the same procedure as that for its chlorinated analogue H(CHB₁₁Cl₁₁),^[12] although the prepa-



Scheme 1. Synthesis of the carborane acid HY (Y = CHB₁₁F₁₁[−]).

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ration of significant amounts of clean product eluded us for a long time. We now understand this difficulty in terms of $\text{H}(\text{CHB}_{11}\text{F}_{11})$ being a considerably stronger acid than $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$, and thus capable of reacting rapidly with all organic species, and being the ultimate desiccant. So, purity of starting materials and the scrupulous exclusion of water were imperative. In particular, we found that the trityl salt of $\text{CHB}_{11}\text{F}_{11}^-$ must be carefully purified by successive recrystallizations from *o*-dichlorobenzene to remove occluded organic compounds. Another critical step was to perform the reaction of $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3][\text{CHB}_{11}\text{F}_{11}]$ with HCl twice (sequentially) to completely remove silane byproducts. Once isolated, small quantities of $\text{H}(\text{CHB}_{11}\text{F}_{11})$ were obtained in high purity by sublimation under high vacuum at about 160°C , a temperature similar to that used for the sublimation of $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$. Otherwise, synthetic amounts were typically made in 100–200 mg batches and, under the best conditions, were estimated, from the virtual absence of νOH in the IR, to contain less than 2% hydrated impurity. In our experience, samples can be stored for no more than a few days, even in a good dry box, before becoming significantly degraded by hydration and/or reaction with trace solvent vapors. Once hydrated, the acid cannot be dehydrated by vacuum sublimation.

$\text{H}(\text{CHB}_{11}\text{F}_{11})$ is expected to be isostructural with $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ and have a linear polymeric structure with two-coordinate, low-barrier H^+ bridging between F atoms. As shown in Figure 1a and b, the IR spectrum is somewhat

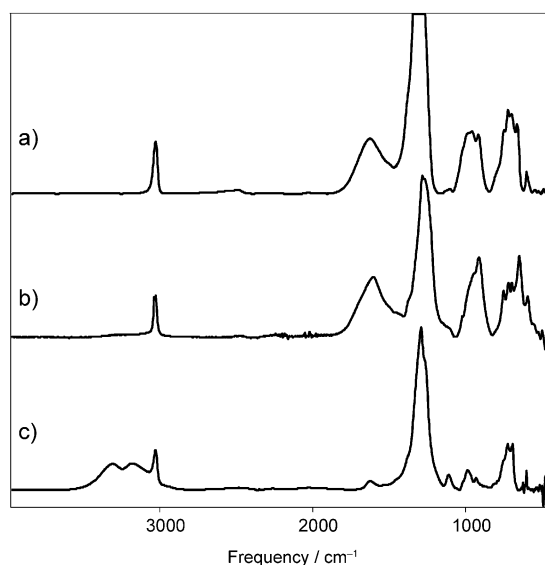


Figure 1. IR spectra of a) $\text{H}(\text{CHB}_{11}\text{F}_{11})$ purified by sublimation, b) $\text{H}(\text{CHB}_{11}\text{F}_{11})$ from bulk synthesis, and c) $[\text{H}_3\text{O}][\text{CHB}_{11}\text{F}_{11}]$ from minimal uptake of water. Spectra (a) and (c) were recorded in transmission mode, (b) in ATR mode.

related to that of the symmetrical bifluoride ion, FHF^- ,^[13] and is diagnostic of low-barrier H-bonding.^[14] Instead of νHF at about 2500 cm^{-1} as might be expected for a terminal $\text{H}-\text{F}$ bond, $\text{H}(\text{CHB}_{11}\text{F}_{11})$ shows a broad band at about 1605 cm^{-1} assigned to νFHF and absorptions in the $1000\text{--}900\text{ cm}^{-1}$ region assigned to δFHF in a nearly symmetrical proton-

bridged structure. The corresponding bands in $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ are at about 1100 and 615 cm^{-1} , respectively.^[11] Deuteration, achieved by stirring the protio acid in liquid DCl , led to the loss of both the 1605 and $1000\text{--}900\text{ cm}^{-1}$ bands. The corresponding νFDF and δFDF bands, expected at about 1140 and $710\text{--}640\text{ cm}^{-1}$ by harmonic oscillator calculations, are both largely masked by the very strong νBB and νBF bands of the anion. Otherwise, the IR spectrum of $\text{D}(\text{CHB}_{11}\text{F}_{11})$ shows only bands expected from the anion: νCH at 3030 cm^{-1} and multiple absorptions centered near 1300 and 700 cm^{-1} from νBB and νBF , respectively.

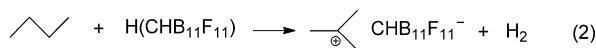
Upon exposure to traces of water vapor, $\text{H}(\text{CHB}_{11}\text{F}_{11})$ is instantly hydrated. With minimal hydration, the IR spectrum (Figure 1c; Supporting Information, Figure S11) is consistent with the formation of an H_3O^+ salt. Broad νOH bands at about 3300 and 3175 cm^{-1} are assigned to ν_s and ν_{as} , respectively. Their frequencies are higher than those in the chlorinated analogue $[\text{H}_3\text{O}][\text{CHB}_{11}\text{Cl}_{11}]$ at $3225, 2910\text{ cm}^{-1}$,^[15] indicating weaker H-bonding of the H_3O^+ ion to the less-basic fluorinated carborane anion. The band at about 1625 cm^{-1} is assigned to $\delta(\text{H}_3\text{O})$. The other major bands in the spectrum are νBB and νBF at circa 1300 and 700 cm^{-1} , respectively.

As expected for such a strong acid, solid $\text{H}(\text{CHB}_{11}\text{F}_{11})$ reacts instantly on contact with benzene to give an isolable benzenium ion salt, $[\text{C}_6\text{H}_7^+][\text{CHB}_{11}\text{F}_{11}^-]$ (for the IR spectrum, see the Supporting Information, Figure S12). The circa 10 cm^{-1} increase in frequency observed for the $\nu(\text{CC}) + \delta(\text{CCH})$ band near 1600 cm^{-1} relative to free benzene is diagnostic of the benzenium ion.^[16] The νCH bands of the acidic $\text{sp}^3\text{ CH}_2$ group occur at low frequency (2818 and 2794 cm^{-1}) owing to $\text{C}-\text{H}\cdots\text{anion}$ H-bonding.^[17] Their frequencies are somewhat higher than that in $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$ (2776 cm^{-1}), consistent with weaker H-bonding to the less-basic fluorinated carborane anion relative to the chlorinated analogue. The structure and remarkable stability of these so-called Wheland intermediates of electrophilic aromatic substitution have been discussed previously.^[16]

In a clear demonstration of the extremely high acid strength of this Brønsted-only acid, we find that $\text{H}(\text{CHB}_{11}\text{F}_{11})$ reacts with alkanes at room temperature, like mixed Brønsted/Lewis acids such as “magic acid” ($\text{HSO}_3/\text{SbF}_5$).^[18] When solid $\text{H}(\text{CHB}_{11}\text{F}_{11})$ is stirred in suspension with *n*-hexane, the appearance of a diagnostic low frequency νCH band at 2758 cm^{-1} in the IR spectrum of the product (the low frequency arising from hyperconjugation and $\text{C}-\text{H}\cdots\text{anion}$ hydrogen bonding)^[17,19] indicates that about 50% of the solid acid is converted into a microcrystalline carbocation salt within 2 h (Supporting Information, Figure S14). This is the expected outcome of protonation of an alkane and elimination of H_2 [Eq. (1)]:



Evolved H_2 was detected by gas chromatography (Supporting Information, Figure S13). A similar protonation experiment with a suspension of $\text{H}(\text{CHB}_{11}\text{F}_{11})$ in liquefied *n*-butane indicates that the acid converts butane into a microcrystalline salt of *tert*-butyl cation [Eq. (2)]:



The distinctive low frequency and shape of the νCH absorptions in the IR spectrum of the product (Supporting Information, Figures S15–S17) closely matches that of known $[\text{tBu}^+][\text{CHB}_{11}\text{Cl}_{11}]^-$,^[17] except that the ν_{max} frequency at 2823 cm^{-1} of the fluorinated anion salt is higher than that of the chlorinated anion salt (2788 cm^{-1}). This is readily understood in terms of weaker C–H⋯anion H-bonding of tBu^+ to the fluorinated anion. The tertiary isomer of butyl cation is the expected result of facile 1,2 shifts from initially formed primary or secondary carbocation-like species.^[20] The X-ray structures of two *tert*-butyl salts with carborane anions have been reported previously.^[17,21]

Additional characterization of these C_4 and C_6 carbocation salts was obtained from reactivity studies with NaH, anticipating two possible outcomes: 1) hydride transfer to reform an alkane; or b) hydride acting as a base, deprotonating the carbocation and forming an alkene.

When a sample of the presumed C_6 carbocation salt, obtained as above from the protonation of *n*-hexane with $\text{H}(\text{CHB}_{11}\text{F}_{11})$, was treated with a NaH in liquid SO_2 , a single hydrocarbon product was detected by gas chromatographic analysis (Supporting Information, Figure S18). Its identity as a C_6 alkene was shown by mass spectroscopy (m/z 84.086; see the Supporting Information, Figure S19). Electron impact fragments corresponding to loss of methyl, ethyl, and propyl groups were observed and comparison of this fragmentation pattern to those catalogued for C_6 alkenes shows the closest match to that of 3,3-dimethyl-1-butene, although it is shares substantial similarity to those of 2-methyl-2-pentene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, and 4-methyl-2-pentene (Supporting Information, Figure S20). Thus, a C_6 carbocation was the product of protonation of *n*-hexane, most likely with a tertiary cationic center arising from the well-known rearrangement of initially formed primary or secondary carbocation-like species to a more stable tertiary cation by rapid 1,2 shifts.^[20]

Under somewhat different experimental conditions, NaH acts as a hydride transfer agent rather than a base. Intimate co-grinding of the presumed C_6 carbocation salt with $\text{NaH}_{(s)}$ led to evolution of four different C_6 alkanes by GC analysis: 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, and 3-methylpentane (Supporting Information, Figure S21). This mixture presumably reflects the rapid rearrangement equilibria possible in all tertiary alkyl cations.^[20] Similarly, intimate co-grinding with $\text{NaH}_{(s)}$ of the tBu^+ salt derived from protonation of *n*-butane led to *iso*-butane as the major alkane detectable by GC/MS in the head space (Supporting Information, Figure S22). *tert*-Butyl cations produced in a different manner,^[22] by protonation of butyl chloride with $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$, behaved in identical fashion.

In contrast to these room-temperature reactions of $\text{H}(\text{CHB}_{11}\text{F}_{11})$ with alkanes, the chlorinated carborane acid $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ scarcely reacts with *n*-hexane or butane under comparable conditions. Even after 24 h stirring as a suspension in *n*-hexane, less than 25 % conversion of $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ into carbocation salts was detected by IR spectroscopy. Thus,

the fluorinated carborane acid is now the strongest pure acid known.

The existence of a Brønsted-only acid that can protonate alkanes at room temperature offers new opportunities for studying acid-catalyzed hydrocarbon chemistry related to hydrocarbon reforming on zeolites at high temperatures. Potential advantages are that a sublimable solid acid is easier to handle than a liquid acid and a Brønsted-only acid is free of the potentially complicating effects of a Lewis acid. Room-temperature access to alkane protonation chemistry should also allow the easier application of investigative techniques that are difficult to apply to zeolites;^[23] the acidity of zeolites is much lower^[24] and their reactions with alkanes must be carried out at high temperatures.^[25] Such room-temperature techniques have already been applied with unexpected results to chloroalkanes, which are more easily protonated than alkanes. Peculiar stoichiometric relationships in reversible, carbocation-like oligomerization sequences were observed.^[22]

Experimental Section

All manipulations were carried out under very dry conditions using Schlenkware or an inert atmosphere glovebox (H_2O , $\text{O}_2 < 0.5\text{ ppm}$). Solvents were dried by standard methods. HF was dried by condensing gaseous HF into a PFA vessel containing potassium hexafluoronickelate. HCl was dried by passing it through a 25 cm column of P_2O_5 plugged at both ends with glass wool. 10 % F_2 in N_2 was used without additional purification. ^1H , ^{11}B , and ^{19}F spectra were obtained on a Bruker Avance 300 MHz spectrometer. Attenuated Reflectance spectra (ATR) IR spectra were run on ABB MB3000 spectrometer in the $525\text{--}4000\text{ cm}^{-1}$ frequency range using a diamond crystal. Mass spectra were collected using a Waters GCT GC/MS operating at 15°C .

$\text{Cs}(\text{CHB}_{11}\text{F}_{11})$: **Caution!** HF and F_2 are extremely toxic and are used under pressure. All reactions should be carried out with appropriate apparatus and safety precautions in a well-ventilated hood using full-body protective clothing and the “buddy” system. Adapting the method of Solntsev and Strauss,^[9] a 300 mL Teflon-lined Monel bomb equipped with a Teflon stir bar was charged with 2 g of $\text{Cs}(\text{CHB}_{11}\text{H}_{11})$ ^[26] and placed in an oven at 80°C for 4 h. It was then connected to a PFA vacuum manifold, evacuated, and cooled to dry ice temperature in a dry ice/methanol bath. Approximately 35 mL of high purity hydrogen fluoride was condensed into the reactor and the reaction was stirred at room temperature for 24 h. After cooling in a dry ice/methanol bath, the reactor was evacuated and then placed on a stainless steel vacuum manifold. 280 PSI (20 bar) of 10 % F_2 in N_2 was introduced into the bomb, sealed, and allowed to warm to room temperature. After stirring for 8 h, the bomb was cooled in a dry ice/methanol bath and the excess pressure vented. The process of adding fluorine, allowing it to react, and venting the reactor was repeated five times. Then, hydrogen fluoride was condensed out of the bomb and the reactor was carefully opened and allowed to stand in the air. After 1 hour, the contents were dissolved in 80 mL of dry acetonitrile and filtered through fine frit, to remove insoluble CsBF_4 . The filtrate was evaporated to dryness on a rotary evaporator, yielding a sticky yellow powder. This powder was placed in an inert atmosphere glove box, suspended in dry dichloromethane (100 mL), and stirred overnight. The suspension was filtered off to yield a white powder, which was dried under vacuum for 1 hour (2.74 g; 80 %). ^1H NMR ($[\text{D}_6]\text{acetone}$): $\delta = 4.35\text{ ppm}$ (s, 1H, CH). ^{11}B NMR ($[\text{D}_6]\text{acetone}$, unreference): $\delta = -7.75$ (s, 1B), 15.86 (s, 5B), 17.09 ppm (s, 5B) (SI, Figure S3). ^{19}F NMR ($[\text{D}_6]\text{acetone}$, unreference): $\delta = -251.59$ (m, 1F), -255.63 ppm (m, 10F) (SI, Figure S2). The completeness of fluorination was initially judged by the absence of νBH bands near

2550 cm⁻¹ in the IR spectrum of the product (SI, Figure S1). ¹⁹F and ¹¹B NMR spectra were found to be less reliable indicators of completeness of fluorination. The most sensitive indicator of anion purity was negative ion electrospray mass spectrometry (SI, Figure S4).

Ag(CHB₁₁F₁₁)·2C₆H₆: Cs(CHB₁₁F₁₁) (2.78 g, 5.87 mmol) and AgNO₃ (4.98 g, 29.93 mmol) were suspended in dry benzene (300 mL) and stirred magnetically. After 24 h, the benzene was decanted and a fresh 300 mL aliquot added to the remaining solids. This process was repeated three times. The combined (3 × 300 mL) benzene fractions were filtered through a fine frit and evaporated to dryness to yield an off-white solid that was dried under vacuum for 1 hour (2.18 g, 83 %). ¹H NMR: (300 MHz, CD₂Cl₂): δ = 3.946 (s, 1H, CH), 7.36 ppm (s, 6H, benzene) (SI, Figure S6). ATR-IR (SI, Figure S5).

[(C₆H₅)₃C][CHB₁₁F₁₁]: In the glove box, Ag(CHB₁₁F₁₁)·2C₆H₆ (2.48 g, 4.14 mmol) and (C₆H₅)₃CBr (1.48 g, 4.55 mmol) were dissolved in 25 mL of dry dichloromethane and stirred overnight. The yellow precipitate of AgBr was filtered off with a fine frit, washing with 5 mL of dichloromethane. The filtrate was evaporated to dryness under vacuum, yielding a bright yellow waxy solid. This was recrystallized twice by layering 10 mL 1,2-dichlorobenzene solutions with 15 mL of hexane. The solid was filtered off and dried under vacuum for 1 h (2.2 g, 89 %). ¹H NMR (300 MHz, CD₂Cl₂): δ = 2.776 (s, 1H, C-H), 7.705, 7.938, 8.325 ppm (phenyl groups) (SI, Figure S8). ATR-IR (SI, Figure S7).

[(Et₃Si)₂H][CHB₁₁F₁₁]: [(C₆H₅)₃C][CHB₁₁F₁₁] (200 mg, 0.342 mmol) was covered with dry 1,2-dichlorobenzene (0.5 mL). To this suspension 1 mL of Et₃SiH was added and the solution stirred for 0.5 h. Dry hexane (5 mL) was added gradually while stirring. The resulting precipitate was filtered and washed with dry hexanes (5 mL) (0.175 g, 89 %). ATR-IR (SI, Figure S9). The broad band at 1873 cm⁻¹ is diagnostic of the hydride-bridged disilyl cation.^[27]

H(CHB₁₁F₁₁): Extra-dry HCl gas was condensed (ca. 2 mL) onto [(Et₃Si)₂H][CHB₁₁F₁₁] (200 mg) using liquid N₂, and the mixture was stirred at 0 °C for 0.5 hour in a sealed heavy-walled Schlenk tube having a wide bore Teflon stopcock below the joint. The HCl was removed under vacuum and a new portion of HCl (2 mL) was added, stirring for 0.5 hour at 0 °C. The HCl allowed to escape anaerobically and the remnant solid was pumped under vacuum for 0.5 h (96 mg, 81 %). The deuterated acid, D(CHB₁₁F₁₁), was prepared by stirring the protio acid in liquid DCl followed by evaporation of DCl/HCl and drying under vacuum. The IR spectrum is compared to the protio form in the Supporting Information, Figure S10.

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