Superacids

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The Strongest Acid: Protonation of Carbon Dioxide

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Abstract: *The strongest carborane acid, $H(CHB_{11}F_{11})$, protonates CO_2 while traditional mixed Lewis/Brønsted superacids do not. The product is deduced from IR spectroscopy and calculation to be the proton disolvate, $H(CO_2)_2^+$. The carborane acid $H(CHB_{11}F_{11})$ is therefore the strongest known acid. The failure of traditional mixed superacids to protonate weak bases such as CO_2 can be traced to a competition between the proton and the Lewis acid for the added base. The high protic acidity promised by large absolute values of the Hammett acidity function (H_0) is not realized in practice because the basicity of an added base is suppressed by Lewis acid/base adduct formation.*

The recent synthesis of the strongest pure acid, the carborane acid $H(CHB_{11}F_{11})$, which can protonate alkanes at room temperature,[1] opens up the possibility of protonating molecules that have not previously been protonated. The most interesting targets are small gaseous molecules, such as H_2, N_2, O_2, CO, CO_2, and atomic Xe. Mass spectral data show that these extremely weak bases can accept a proton in the gas phase to form stable cations.[2–9] Protonated CO_2 has been observed in the gas phase by infrared spectroscopy,[10,11] solvated by a noble gas,[12] and is a confirmed interstellar species.[13,14] On the other hand, demonstrating protonation in condensed phases presents a much greater challenge. Gillespie and Pez[3] could find no evidence for the protonation of these gases in a $HSO_3F/SbF_5/SO_3$ "magic acid" system, one of the strongest known mixed Brønsted/Lewis acids. Drews and Seppelt[15] could find no evidence for the involvement of HXe^+ in the formation of the Xe_2^+ ion in the somewhat stronger HF/SbF_5[16] mixed acid system. Olah and Shen[17] found indirect evidence for the protonation of Xe and CO_2 in HF/SbF_5 by observing slowed rates of H exchange into D_2 when these gases were present. The necessity of HXe^+ and HCO_2^+ ions as reaction intermediates was postulated. Gladysz and Horváth et al.[18] produced the first evidence for the existence of protonated carbon monoxide in condensed media by assigning a sharp peak in the ^{13}C NMR spectrum at 139.5 ppm and a very broad IR band near 2110 cm^{-1} to the formyl cation, HCO^+, when CO was dissolved in HF/SbF_5 at high pressures. This evidence is considered strong but not conclusive.[19]

The question of whether carborane acids are better than traditional mixed Lewis/Brønsted superacids at protonating small gaseous molecules boils down to two practical issues: acid strength and reaction conditions. Carborane acids are solids with proton-bridged polymeric structures,[20] so their reactions with gases are hampered by slow kinetics at the solid/gas interface. High gas pressures may ameliorate this problem by converting the gas into a liquid or a supercritical fluid, and the observation by IR that $H(CHB_{11}F_{11})_{(s)}$ appears to partially convert liquefied methane into *tert*-butyl cation-like salts is encouraging in this regard.[21] The alternative approach of dissolving a carborane acid in a solvent necessarily, and undesirably, levels acidity down to that of the protonated solvent. Carborane acids are quite soluble in liquid SO_2, presumably because of the formation of the proton disolvate, $H(SO_2)_2^+$,[22] but none of the aforementioned gases have sufficient basicity or solubility to compete with SO_2 for protonation.[23]

The issue of whether carborane acids can protonate weakly basic molecules more easily than traditional mixed Lewis/Brønsted acids goes to the heart of the question of which class of acids can claim the title to the strongest acids.[24] Traditional mixed acids are liquids and therefore lend themselves to quantitative description in terms of the H_0 Hammett acidity function.[16] On the other hand, carborane acids are solids and rely on the νNH scale.[25] We draw attention to the poorly recognized phenomenon of basicity suppression,[26] whereby the Lewis acid in a mixed acid can form an adduct with an added base, thereby lowering the intrinsic basicity of that base, and making it harder to protonate. An alternative way to view this phenomenon is to recognize that in any mixed acid there will always be a competition between H^+ and the Lewis acid for an added base. Thus, Brønsted acidity in a mixed acid, as indicated by H_0 (or pH)[27] is, in practice, unavailable for protonation of an added base. For this reason, we take a pragmatic approach to deciding which acid is the strongest. The strongest acid will simply be that which successfully protonates the weakest base. As we shall see below, the strongest carborane acid protonates CO_2 while traditional mixed Brønsted/Lewis superacids do not. Therefore, carborane acids are, in practice, shown to be the strongest acids.

Using sapphire NMR tube technology,[18] CO_2 was condensed onto ground $H(CHB_{11}F_{11})$[1] at liquid N_2 temperatures. Upon warming to room temperature to obtain CO_2 as a liquid, the crystalline form of the acid was observed to change its aggregation appearance. After gas removal, evacuation at 50 mTorr to remove possible physisorbed species, and back filling with dinitrogen, the IR spectrum of the solid showed the appearance of a sharp band at 2365 cm^{-1}

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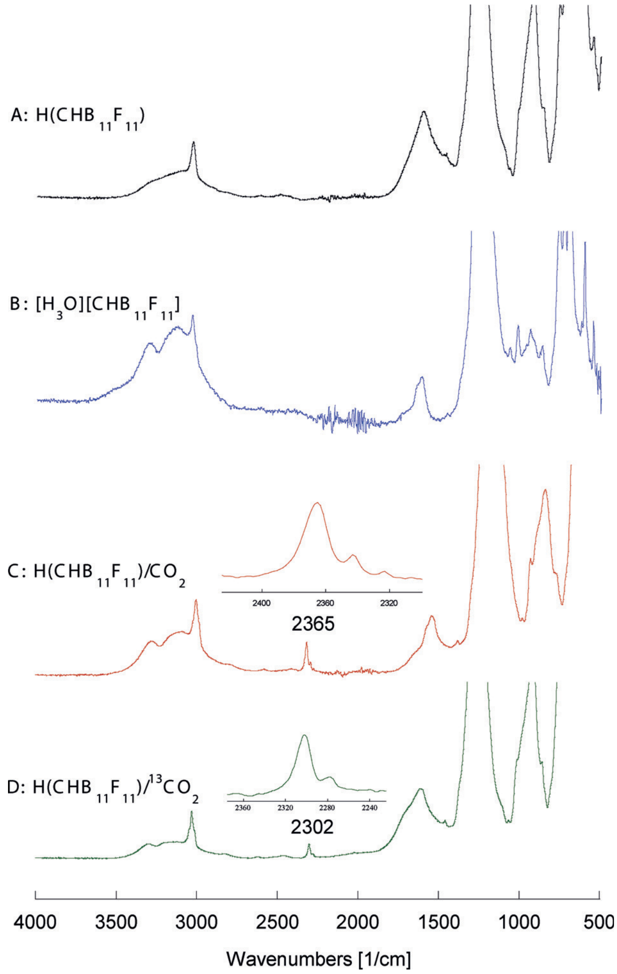

Figure 1. IR spectra of A) $H(CHB_{11}F_{11})$ containing a small amount of $[H_3O][CHB_{11}F_{11}]$, B) $[H_3O][CHB_{11}F_{11}]$, C) $H(CHB_{11}F_{11})$ exposed to natural abundance CO_2, with expanded scale insert of ν_{asym} CO, and D) $H(CHB_{11}F_{11})$ exposed to 99%-enriched $^{13}CO_2$, with expanded scale insert.

and a weaker band at 2343 cm^{-1} (Figure 1 c), assigned to the in-phase and out-of-phase ν_{asym} stretches of protonated CO_2. When the same experiment was carried out with 99 % ^{13}C-labelled CO_2, appropriate red shifts to 2302(s) and 2276(w) cm^{-1} (Figure 1 d) were observed. These shifts of 63 and 67 cm^{-1}, respectively, are consistent with the 65 cm^{-1} ^{13}C isotope shift obtained for ν_{asym} (2349 cm^{-1}) in matrix isolated CO_2.[28,29] IR bands of the starting acid (νFHF ca. 1605 cm^{-1} and δFHF 900–1000 cm^{-1}; Figure 1 a) remain present, indicating only partial reaction. This is presumably the result of restricted penetration of CO_2 through the reacting surface layer of the solid acid. The spectrum also shows increased intensity of bands from $[H_3O][CHB_{11}F_{11}]$ (broad νOH ca. 3300 and 3175 cm^{-1} and δH_3O at ca. 1625 cm^{-1}, Figure 1 b), an inevitable contaminant arising from the presence of trace water. There is no observable reaction of CO_2 with pure hydrated acid, $[H_3O][CHB_{11}F_{11}]$. Allowing longer reaction times and heating the reaction to higher temperatures, where liquid CO_2 goes supercritical, gave similar results but with increased contamination by water. Similar experiments exposing the undeca-chloro carborane acid, $H(CHB_{11}Cl_{11})$, to CO_2 showed barely detectable bands in the 2370–2340 cm^{-1} region, consistent with lower reactivity of this somewhat weaker carborane acid.[25]

The Raman active ν_{sym} vibration of free CO_2 at 1384 cm^{-1} is expected to become IR active in a protonated product. Although this region is masked by strong νBB bands from the anion, computer subtraction of remnant acid revealed two possible bands centered at 1325 cm^{-1} and 1295 cm^{-1} (Supporting Information, Figure S2) which are attributed to the in-phase and out-of-phase symmetric C=O stretches, respectively. Computer subtraction of the acid from the resulting spectrum of protonated $^{13}CO_2$ exposes a peak at 1293 cm^{-1} with a shoulder at 1324 cm^{-1} (Figure S3). The small observed isotopic shift in ν_{sym} of 1–3 cm^{-1} is consistent with free CO_2 (Δ18 cm^{-1})[30] and calculated values of approximately 1 cm^{-1} (see below). Similarly, bending vibrations expected in the region of the degenerate δ bands of free CO_2 at 662 cm^{-1}[28] are masked by strong νBF bands of the anion but computer subtraction of remnant acid revealed absorptions near 690 cm^{-1}.

Attempts to obtain a Raman spectrum using 785 nm excitation were unsuccessful owing to fluorescence from the carborane anion. ^{13}C CPMAS NMR spectroscopy was equally uninformative owing to low signal to noise.

The solid product is stable to loss of CO_2 upon evacuation but, as indicated by the observation of gas bubbles upon addition of an arene solvent, CO_2 can be displaced by a stronger base. Treatment of the ^{13}C-enriched solid with benzene released head gas into the reaction vessel that was shown by mass spectrometry to have $^{13}CO_2$ enriched well above natural abundance (Figure S4). The resulting solid showed no IR bands attributable to CO_2. Bands characteristic of the benzenium ion salt $[C_6H_7][CHB_{11}F_{11}]$,[1] including low frequency νCH bands near 2800 cm^{-1} and the ν(CC) + δ-(CCH) band at 1605 cm^{-1}, were observed (Figure S6).

What is the structure of protonated CO_2? It is most *un*likely to be the result of simple protonation, that is, a monoprotonated salt of composition $[HCO_2][CHB_{11}F_{11}]$. A major lesson learned from recent studies on the nature of H^+ in condensed media is the prevalence of proton di-solvation.[31] This must be connected to the observation in the gas phase, that the energetics of disolvation are remarkably constant, whereas those of monosolvation (that is, proton affinity) are highly variable.[32] The monosolvated HCO_2^+ ion should show a single ν_{asym}CO band, but two are observed (Figure 1 c,d inserts). In the gas phase, νOH for the HCO_2^+ ion is observed at 3375 cm^{-1}.[13,33] In a solid phase salt with $CHB_{11}F_{11}^-$ as counterion, H-bonding to the anion would be expected to broaden and lower this frequency into the 3200–2900 cm^{-1} region. The spectrum of the product (Figure 1 c) shows no obvious candidate for this band, even with computer subtraction of bands from $[H_3O][CHB_{11}F_{11}]$ (Figure S7). So there is no evidence for the presence of the HCO_2^+ ion.

The anticipated product of CO_2 protonation is a disolvate containing the $H(CO_2)_2^+$ ion, particularly considering that CO_2 is present in large excess [Eq. (1)].

$$2\,CO_{2(l)} + H(CHB_{11}F_{11})_{(s)} \rightarrow [H(CO_2)_2][CHB_{11}F_{11}]_{(s)} \tag{1}$$

Such a proton disolvate is expected to have linear two-coordination at H^+ and show the characteristics of short, strong, low-barrier (SSLB), symmetrical (or nearly symmetrical) H-bonding.[31,34–36] However, confirming the presence of the disolvated ion is not as simple as disproving the presence of the monosolvated ion. The νOHO stretch of a low-barrier H-bond is expected to be a broad absorption near 1600 cm^{-1},[31] in exactly the same region of the IR spectrum as νFHF of the starting material acid and δOH of the H_3O^+ contaminant. Because of these overlapping broad bands, computer deconvolution is not reliable. Higher degrees of solvation, such as a trisolvate $H(CO_2)_3^+$ or entropically disfavored cyclic structures, are so unlikely that they can be excluded.

Calculated geometries for HCO_2^+ and $H(CO_2)_2^+$ ions were determined using density functional theory (DFT) at the B3LYP level because of its agreement with experimental for SSLB H-bonding.[37] High level electronic structure calculations were also performed using the coupled cluster singles and doubles method (CCSD).[38] The correlation consistent aug-cc-pvtz basis set was used for all calculations.[39–41] Consistent with previous ab initio MP2 studies[42–44] protonation is expected to occur at an O-atom sp^2 lone pair. The DFT results suggest $H(CO_2)_2^+$ exists as a symmetric cation, while an imaginary frequency at the CCSD level suggests that the symmetrical $H(CO_2)_2^+$ ion is a transition state corresponding to interconversion of two related slightly asymmetric geometries (Figure 2). The energy barrier between the asymmetrical and symmetrical transition state is calculated to be less than 0.25 kcal mol^{-1}, in accordance with SSLB theory.

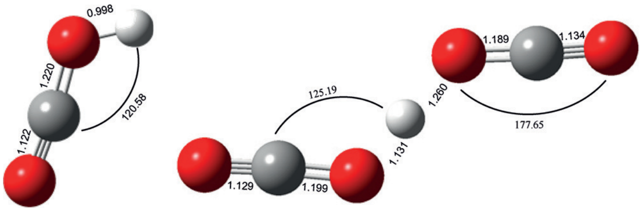

Figure 2. The CCSD calculated structures of the $H(CO_2)^+$ and $H(CO_2)_2^+$ ions. For further bond lengths and angles, see the Supporting Information.

Relevant calculated vibrational frequencies for gas phase HCO_2^+ and $H(CO_2)_2^+$ ions are compared in Table 1. The symmetrical structure is proposed to have one IR and one Raman active ν_{asym} C=O stretch. Breaking the symmetry results in both ν_{asym} stretches being IR active, consistent with experimental results. Two comments need to be made. With respect to ν_{asym}, it is unusual for a frequency to increase upon protonation. However, the increase is small and it closely follows the 5–24 cm^{-1} increases in ν_{asym} observed when CO_2 coordinates to various divalent metal ions in zeolites,[45] and in gas phase protonation of CO_2.[43] In fact, ν_{asym} of free CO_2 is quite insensitive to protonation as either HCO_2^+ or $H(CO_2)_2^+$, reflecting both the weak basicity of CO_2 and its large HOMO–LUMO gap. Furthermore, CCSD frequency calculations are expected to be somewhat higher than experimental results owing to the use of the harmonic oscillator model. While scaling factors can be used to correct this systematic error in the gas phase, they are not as useful in condensed phases because of the unpredictable effects of H-bonding and ion–ion interactions. Regardless, the calculations and previous experimental data clearly support the disolvate formulation.

Table 1: IR frequencies (cm^{-1}) for $H(CO_2)^+$ and $H(CO_2)_2^+$.[a]

	ν_{asym}(CO)	ν_{sym}(CO)	δ(OCO)
Obsd. free CO_2[28,30]	2351, 2349	1388, 1285	664
Obsd. free $^{13}CO_2$[28,30]	2285, 2283	1370, 1266	649
Calcd. $H(CO_2)^+$	2483	1264	547
	Symmetrical Disolvate		
Calcd. $H(CO_2)_2^+$	2471	1330	634
Calcd. $H(^{13}CO_2)_2^+$	2403	1329	614
	Asymmetrical Disolvate		
Calcd. $H(CO_2)_2^+$	2477, 2472	1379, 1323	701
Calcd. $H(^{13}CO_2)_2^+$	2408, 2404	1379, 1322	685
Obs. $H(CO_2)_2^+$	2365	~1325, 1295	690
Obs. $H(^{13}CO_2)_2^+$	2302	~1293	692

[a] CCSD calculated values are unscaled. For detailed intensities, see the Supporting Information, Tables S3–S5.

In conclusion, CO_2 is protonated by the strongest known carborane acid, $H(CHB_{11}F_{11})$, and the product is the proton di-solvate, $H(CO_2)_2^+$. That carborane acids can protonate CO_2, but traditional superacids cannot, shows that carborane acids are the strongest acids known. They have therefore earned the superacid name. The failure of traditional mixed Lewis/Bronsted superacids to protonate weak bases, such as CO_2, can be traced to the competitive presence of the Lewis acid. Present in high concentration, the Lewis acid in a mixed superacid forms adducts with added bases and protonation cannot compete. Despite the promise of high acidity in the Hammett acidity functions of mixed acids, high Brønsted acidity cannot be realized in practice and the basicity of weakly basic molecules has been systematically underestimated. The Lewis basicity of CO_2 underlies some remarkable reaction chemistry involving both main group[46,47] and transition metal elements.[48] The present demonstration of its Brønsted basicity may offer new opportunities for further functionalization.

Experimental Section

All manipulations were carried out under the driest possible conditions using flamed glassware and inert atmosphere gloveboxes (H_2O, $O_2 < 0.5$ ppm). Solvents were dried by standard methods. Carbon dioxide was obtained from Sigma Aldrich (99.95% purity), the labeled $^{13}CO_2$ having 99% ^{13}C and < 2% ^{18}O. Attenuated Reflectance (ATR) IR spectra were run on either an ABB MB3000 or a PerkinElmer Spectrum 1 spectrometer (housed in a drybox) in the 4000–525 cm^{-1} frequency range using a diamond crystal. Mass spectra were collected using a Waters GCT GC/MS. Sapphire NMR tubes rated for internal pressures of 500 atm were purchased from Wilmad glass. They were glued to Swagelock stainless steel adapters with Epoxy and connected to the gas supply using silicone and nylon gaskets. **CAUTION!** The present experiments result in very high gas pressures. Working behind an explosion shield is recommended at all times. Despite the strength of sapphire, one explosion did occur. This was ascribed to multiple usage of the tube and aging of the Epoxy glue used to secure the Swagelock fixtures.

$H(CHB_{11}F_{11})$ was synthesized on a 100–200 mg scale by the published method[1] and checked for minimal hydration by IR prior to use. Samples (ca. 35 mg) were pulverized with a teflon-coated stir bar in a small vial and loaded into a sapphire tube using a glass capillary as a funnel. After secure closure, connection to a stainless steel Schlenk line and appropriate evacuation, CO_2 was condensed onto the sample with liquid nitrogen cooling, visually assessing a volume of ca. 0.4 mL at room temperature. The solid did not display observable solubility but did aggregate into chunks. After 10 min, CO_2 was removed under vacuum (pumping at ca. 50 mTorr for > 2 min) and the IR of the solid was recorded immediately. The same reaction was performed with $^{13}CO_2$. The reaction was also performed in supercritical CO_2 by heating the sapphire tube in a water bath at 41 °C for 10 min and at 45 °C for 72 h. $H(CHB_{11}Cl_{11})$[49] was reacted with $CO_{2(l)}$ at room temperature for 10 min and with $CO_{2(sc)}$ at 80 °C overnight. The reaction of $H(CHB_{11}F_{11})$ product (8 mg) with benzene (75 μL) was performed in septum-sealed 1 mL vial in a drybox prior to transportation to the mass spectrometer.

Geometry and frequency calculations were carried out by DFT at the B3LYP/aug-CC-PVTZ and CCSD/aug-CC-PVTZ levels using Gaussian 15.[50]

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