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The Strongest Acid. Protonation of Carbon Dioxide

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Abstract: The strongest carborane acid, H(CHB11F11), protonates CO2 whereas traditional mixed Lewis/Brønsted superacids such as "magic acid" do not. The product is deduced from IR spectroscopy and calculation to be the proton disolvate, H(CO2)2+.[22] The carborane acid H(CHB11F11) is therefore the strongest known acid. The failure of traditional mixed superacids to protonate weak bases such as CO2 can be traced to a competition between the proton and the Lewis acid for the added base. The strong acidity therefore promises large absolute values of the Hammett acidity function (H0). The carborane acid H(CHB11F11) is therefore the strongest known acid. The failure of traditional mixed acids to protonate CO2 can be traced to a competition between the proton and the Lewis acid for the added base. The strong acidity therefore promises large absolute values of the Hammett acidity function (H0).

The recent synthesis of the strongest pure acid, the carborane acid H(CHB11F11), which can protonate alkanes at room temperature,[1] opens up the possibility of protonating molecules that haven’t been protonated before. The most interesting targets are small gaseous molecules such as H2, N2, O2, CO, CO2 as well as atomic Xe. Mass spectral data show that these extremely weak bases can add a proton in the gas phase to form stable cations.[2–5] Protonated CO2 has been observed in the gas phase via infrared spectroscopy,[6,11] solvated by a noble gas,[22] and as a confirmed interstellar species.[13,14] On the other hand, demonstrating protonation in condensed phases presents a much greater challenge. Gillespie and Pez[23] could find no evidence for the protonation of these gases in a HSO3F/SbF5/CO2 "magic acid" system, one of the strongest known mixed Brønsted/Lewis acids. Drews and Seppelt[15] found no evidence for the involvement of HXe+ in the formation of the Xe+ ion in the somewhat stronger HF/SbF5 mixed acid system. Ola and Sheh[16] found indirect evidence for the protonation of Xe and CO2 in HF/SbF5 by observing slowed rates of H exchange into D2 when these gases were present. The necessity of HXe+ and HCO2+ 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 13C 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/SbF5 at high pressures. This evidence is considered "strong but not conclusive".[19]

The question of whether carborane acids are better than traditional mixed Lewis/Bronsted superacids at protonating small gaseous molecules boils down to two practical issues: acid strength and reaction conditions. Carborane acids are solids and rely on the protonated solvent. Carborane acids are quite soluble in liquid SO2, presumably because of the formation of the proton disolvate, H(SO2)2+. The carborane acid H(CHB11F11) is therefore the strongest known acid. The failure of traditional mixed acids to protonate weak bases such as CO2 can be traced to a competition between the proton and the Lewis acid for the added base. The high proton acidity promised by large absolute values of the Hammett acidity function (H0) is not realized in practice because the basicity of an added base is suppressed by Lewis acid/base adduct formation.

This evidence is considered "strong but not conclusive". The issue of whether carborane acids can protonate weakly basic molecules more easily than traditional mixed Lewis/Bronsted acids goes to the heart of the question of which class of acids can claim title to the strongest acids.[24] Traditional mixed acids are liquids and therefore lend themselves to quantitative description in terms of the H0 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+/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 CO2 whereas 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] CO2 was condensed onto ground H(CHB11F11) at liq. N2 temp. Upon warming to room temperature to obtain CO2 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\(^{-1}\) and a weaker band at 2343 cm\(^{-1}\) (Fig. 1c), assigned to the in-phase and out-of-phase νasym stretches of protonated CO2. When the same experiment was carried out with 99% 13C-labelled CO2, appropriate red shifts to 2302(s) and 2276(w) cm\(^{-1}\) (Fig. 1d) were observed. These shifts of 63 and 67 cm\(^{-1}\) respectively, are entirely consistent with the 65 cm\(^{-1}\) 13C isotope shift obtained for νasym (2349 cm\(^{-1}\)) in matrix isolated CO2.[28,29] IR bands of the starting acid (νOH ca. 1605 cm\(^{-1}\) and 3600-1000 cm\(^{-1}\), Fig. 1a) remain present, indicating only partial reaction. This is presumably the result of restricted penetration of CO2 through the reacting surface layer of the solid acid. The spectrum also shows increased intensity of bands from [H4O][CHB11F11] (broad νOH ca. 3300 and 3175 cm\(^{-1}\) and νH2O at ca. 1625 cm\(^{-1}\), Fig. 1b), an inevitable contaminant arising from the presence of trace water. There is no observable reaction of CO2 with pure hydrated acid, [H2O][CHB11F11]. Allowing longer reaction times and heating the reaction to higher temperatures, where liquid CO2 goes supercritical, gave similar results but with increased contamination by water. Similar experiments exposing the undeca-chloro carborane acid, H(CHB11Cl11), to CO2 showed barely detectable bands in the 2370-2340 cm\(^{-1}\) region, consistent with lower reactivity of this somewhat weaker carborane acid.[23]

The Raman active νasym vibration of free CO2 at 1384 cm\(^{-1}\) is expected to become IR active in a protonated product. Although this
region is masked by strong vBB bands from the anion, computer subtraction of remnant acid revealed two possible bands centered at ca. 1325 cm\(^{-1}\) and ca. 1295 cm\(^{-1}\) (Fig. 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\(^{-1}\) (Fig. S3). The small observed isotopic shift in \(\nu_{asym}\) of 1-3 cm\(^{-1}\) is consistent with free \(^{13}\)CO\(_2\) (\(\Delta18\) cm\(^{-1}\)\(^{30}\)) and calculated values of ca. 1 cm\(^{-1}\) (see below). Similarly, bending vibrations expected in the region of the degenerate \(\nu_{BB}\) bands of free \(^{13}\)CO\(_2\) at 662 cm\(^{-1}\)\(^{28}\) are masked by strong vBB bands of the anion but computer subtraction of remnant acid revealed absorptions near 690 cm\(^{-1}\).

What is the structure of protonated CO\(_2\)? It is most unlikely to be the result of simple protonation, i.e., 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 (i.e., proton affinity) are highly variable.\(^{12}\) The monosolvated HCO\(_2^+\) ion should show a single \(\nu_{asym}\) CO band but two are observed (Fig. 1c, 1d inserts). In the gas phase, \(\nu_{OH}\) for the HCO\(_2^+\) ion is observed at 3375 cm\(^{-1}\)\(^{13,33}\). In a solid phase salt with CHB\(_{11}\)F\(_{11}\) as countercation, 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 (Fig. 1c) shows no obvious candidate for this band, even with computer subtraction of bands from [H\(_2\)O][CHB\(_{11}\)F\(_{11}\)] (Fig. 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\(_2\))\(^{+}\) ion, particularly considering that CO\(_2\) is present in large excess (Eq. 1).

\[
2\text{CO}_2(g) + \text{H(CHB}_{11}\text{F}_{11}) \rightarrow [\text{H(CO}_2^+)]\text{[CHB}_{11}\text{F}_{11}]_{\text{sol}}
\]  

(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 \(\nu_{OH}\) 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 vHF of the starting material acid and \(\delta_{OH}\) of the H\(_2\)O contaminant. Because of these overlapping broad bands, computer deconvolution is not reliable. Higher degrees of solvation such as a trisolvate, H(CO\(_2\))\(^{2+}\), or entropically disfavored cyclic structures, are so unlikely 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.\(^{17}\) 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 \textit{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 as illustrated in Fig 2. The energy barrier between the asymmetrical and symmetrical transition state is calculated to be less than 0.25 kcal/mol, in accordance with SSLB theory.

![Figure 1. IR spectra of (A) H(CHB\(_{11}\)F\(_{11}\)) containing a small amount of [H\(_2\)O][CHB\(_{11}\)F\(_{11}\)], (B) [H\(_2\)O][CHB\(_{11}\)F\(_{11}\)], (C) H(CHB\(_{11}\)F\(_{11}\)) exposed to natural abundance CO\(_2\), with expanded scale insert of \(\nu_{asym}\) CO, and (D) H(CHB\(_{11}\)F\(_{11}\)) exposed to 99%-enriched \(^{13}\)CO\(_2\), with expanded scale insert.](image1)

![Figure 2. The CCSD calculated structures of the H(CO\(_2\))\(^{+}\) and H(CO\(_2\))\(^{2+}\) ions. For further bond lengths and angles see Supp. Info.](image2)
Relevant calculated vibrational frequencies for gas phase \( \text{HCO}_2^+ \) and \( \text{H(CO}_2)_2 \) ions are compared in Table 1. The symmetrical structure is proposed to have one IR and one Raman active \( \nu_{\text{asym}} \) stretch. Breaking the symmetry results in both \( \nu_{\text{asym}} \) stretches being IR active, consistent with experimental results. Two comments need to be made. With respect to \( \nu_{\text{asym}} \) 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 \( \nu_{\text{asym}} \) observed when CO\(_2\) coordinates to various divalent metal ions in zeolites\(^{[45]}\) and in gas phase protonation of CO\(_2\)^{[46]} In point of fact, \( \nu_{\text{asym}} \) of free CO\(_2\) is quite insensitive to protonation as either \( \text{HCO}_2^+ \) or \( \text{H(CO}_2)_2^+ \), reflecting both the weak basicity of CO\(_2\) and its large HOMO-LUMO gap. In addition, CCSD frequency calculations are expected to be somewhat higher than experimental results due 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. Regarding the calculations and previous experimental data clearly support the disolvate formulation.

### Table 1. IR frequencies (cm\(^{-1}\)) for \( \text{HCO}_2^+ \) and \( \text{H(CO}_2)_2^+ \). CCSD calculated values are unscaled. For detailed intensities, see S3-S5.

<table>
<thead>
<tr>
<th>( \nu_{\text{sym}}(\text{CO}) )</th>
<th>( \nu_{\text{asym}}(\text{CO}) )</th>
<th>( \delta(\text{OCO}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obsd. free ( \text{CO}_2 ) ( ^{13}\text{C} )</td>
<td>2351, 2349</td>
<td>1388, 1285</td>
</tr>
<tr>
<td>Obsd. free ( \text{CO}_2 )</td>
<td>2285, 2283</td>
<td>1370, 1266</td>
</tr>
<tr>
<td>Calcd. ( \text{H(CO}_2)_2 )</td>
<td>2483</td>
<td>1264</td>
</tr>
<tr>
<td>Calcd. ( \text{H(CO}_2)_2 ) ( ^{13}\text{C} )</td>
<td>2471</td>
<td>1330</td>
</tr>
<tr>
<td>Calcd. ( \text{H(CO}_2)_2 ) ( ^{13}\text{C} ) ( ^{13}\text{C} )</td>
<td>2403</td>
<td>1329</td>
</tr>
<tr>
<td>Calcd. ( \text{H(CO}_2)_2 ) ( ^{13}\text{C} ) ( ^{13}\text{C} )</td>
<td>2477, 2472</td>
<td>1379, 1233</td>
</tr>
<tr>
<td>Calcd. ( \text{H(CO}_2)_2 ) ( ^{13}\text{C} ) ( ^{13}\text{C} )</td>
<td>2408, 2404</td>
<td>1379, 1222</td>
</tr>
<tr>
<td>Obs. ( \text{H(CO}_2)_2 ) ( ^{13}\text{C} ) ( ^{13}\text{C} )</td>
<td>2365</td>
<td>-1325, 1295</td>
</tr>
<tr>
<td>Obs. ( \text{H(CO}_2)_2 ) ( ^{13}\text{C} ) ( ^{13}\text{C} )</td>
<td>2302</td>
<td>-1293</td>
</tr>
</tbody>
</table>

In conclusion, CO\(_2\) is protonated by the strongest known carborane acid, \( \text{H(CHB}_11\text{Cl}_11)_2 \), and the product is the protonated \( \text{H(CHB}_11\text{Cl}_11)_2^+ \), reflecting both the weak basicity of CO\(_2\) and its large HOMO-LUMO gap. In addition, CCSD frequency calculations are expected to be somewhat higher than experimental results due 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.

### Experimental Section

**General.** All manipulations were carried out under the driest possible conditions using flameless glassware and inert atmosphere gloveboxes (\( \text{H}_2\), \( \text{O}_2 <0.5 \text{ ppm} \)). Solvents were dried by standard methods. Carbon dioxide was obtained from Sigma Aldrich (99.95% purity), the labeled \( ^{13}\text{CO}_2 \) having 99% \(^{13}\text{C} \) and 2% \(^{13}\text{O} \). Attenuated Reflectance spectra (ATR) IR spectra were run on either an ABB MB3000 or a Perkin Elmer 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.

\( \text{H(CHB}_11\text{Cl}_11)_2 \) was synthesized on a 100-200 mg scale via the published method\(^{[50]}\) and checked for minimal hydration by IR prior to use. Samples (ca. 35 mg) were pulivered 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 \( ^{13}\text{CO}_2 \). 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. \( \text{H(CHB}_11\text{Cl}_11)_2 \) was reacted with CO\(_2\) at room temp. for 10 min and with CO\(_{\text{box}}\) at 80 °C overnight. The reaction of \( \text{H(CHB}_11\text{Cl}_11)_2 \) product (8 mg) with benzene (75 mL) 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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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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The proton affinity of SO$_2$ is 161.5 kcal/mol. The proton affinities of Xe, CO$_2$, CH$_4$, CO and CS$_2$ are 118.5, 130.9, 131.9, 141.9 and 128.4 kcal/mol, respectively.

See Fig. S9.
Abstract: The strongest carborane acid, H(CHB_{11}F_{11}), protonates CO\textsubscript{2} whereas traditional mixed Lewis/Brønsted acids such as “magic acid” do not. The product is deduced from IR spectroscopy and calculation to be the proton disolvate, H(CO\textsubscript{2})\textsuperscript{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\textsubscript{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\textsubscript{0}) is not realized in practice because the basicity of an added base is suppressed by Lewis acid/base adduct formation.