Investigating the Weak to Evaluate the Strong: An Experimental Determination of the Electron Binding Energy of Carborane Anions and the Gas phase Acidity of Carborane Acids

Matthew M. Meyer,[†] Xue-Bin Wang,[‡] Christopher A. Reed,*,[§] Lai-Sheng Wang,*,[‡,ǁ] and Steven R. Kass*,[†]

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, Department of Physics, Washington State University, Richland, Washington 99354, Chemical & Materials Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, and Department of Chemistry, University of California, Riverside, California 92521-0403

Received October 20, 2009; E-mail: kass@umn.edu; Lai-Sheng_Wang@Brown.edu; chris.reed@ucr.edu

Carborane acids are a new class of Lewis acid free superacids notable for their "strong yet gentle" properties.[1,2] Qualitative measures of their acidity on the mesityl oxide $\Delta\delta^{13}C$ NMR scale[3] and their anion basicity on the trioctylammonium salt νNH infrared scale[4] place $H(CHB_{11}Cl_{11})$ as the current strongest isolable acid in condensed media.[5,6] DFT calculations support this ranking for the gas phase.[5,7,8] Herein, we address the problem of quantifying the gas-phase deprotonation enthalpy of carborane acids experimentally. We also measure the electron binding energy of the $CHB_{11}Cl_{11}^-$ conjugate base to probe the exceptional chemical inertness that accompanies its low basicity. Comparisons are made to the bis(nonafluorobutane-1-sulfonyl)imide ion, $(1-C_4F_9SO_2)_2N^-$, whose conjugate acid is currently the strongest gas phase acid to be determined experimentally.[9]

Five $CHB_{11}X_6Y_5^-$ carborane anions from the series X = Br, Cl, I and Y = H, Cl, CH_3 were readily generated in a Fourier transform mass spectrometer (FTMS) by electrospray ionization of aqueous methanolic solutions of the corresponding cesium salts.[10] Each anion was allowed to react with a series of Brønsted acids of known strength including CF_3SO_3H ($\Delta H^\circ_{acid} = 305.4 \pm 2.2$ kcal mol^{-1})[11] and $(1-C_4F_9SO_2)_2NH$ ($\Delta H^\circ_{acid} = 291.1 \pm 2.2$ kcal mol^{-1}),[9] but no reactions were observed indicating that the proton affinities of all five anions are less than 291.1 ± 2.2 kcal mol^{-1}. These results indicate that the corresponding carborane acids are more acidic than $(1-C_4F_9SO_2)_2NH$, which is currently the strongest measured acid in the gas phase. To verify these bracketing results and rule out the possibility of a kinetic barrier which could preclude the observation of an exothermic proton transfer reaction, the reverse process between $H(CHB_{11}Cl_{11})$ and the $(1-C_4F_9SO_2)_2N^-$ anion was examined. The carborane acid was introduced into an FTMS with the aid of a solid probe inlet and was found to readily protonate $(1-C_4F_9SO_2)_2N^-$ (m/z 580) at 298 K to afford $CHB_{11}Cl_{11}^-$ (m/z 519). Some $1-C_4F_9SO_2NH^-$ (m/z 298) also was observed (Figure 1). Given that proton transfer is observed only in one direction, the lower basicity of the undecachlorocarborane anion relative to $(1-C_4F_9SO_2)_2N^-$ must be of thermodynamic origin. This allows us to confidently assign $\Delta H^\circ_{acid}[H(CHB_{11}Cl_{11})] < 291.1 \pm 2.2$ kcal mol^{-1} which is consistent with B3LYP/6-311+G(d,p)[12] and G3(MP2)[13] predictions at 298 K of 237.6 and 238.3 kcal mol^{-1}, respectively. Protonation is calculated to occur on chlorine which is in accord with the reported X-ray structure and IR spectrum of the acid.[14]
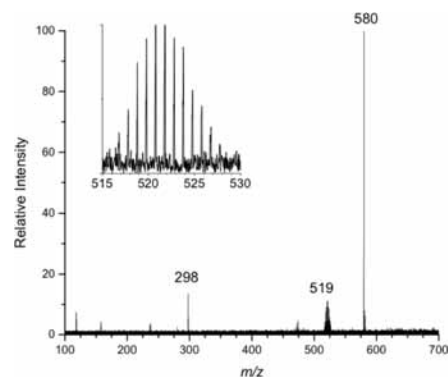
Figure 1. Mass spectrum of the reaction of $(1-C_4F_9SO_2)_2N^-$ (m/z 580) with $H(CHB_{11}Cl_{11})$. The inset is an expansion of the $CHB_{11}Cl_{11}^-$ anion (m/z 519) that reveals the complex isotopic envelope resulting from a species with 11 B and 11 Cl atoms.

To investigate both the basicity and the redox inertness of these remarkable anions, all five carborane anions were reacted with several reference electron transfer reagents with known electron affinities. No reactions were observed with nitrogen dioxide (NO_2, EA = 2.273 ± 0.005 eV), 2-chloroacrylonitrile ($CH_2=C(Cl)CN$, vertical detachment energy (VDE) = 4.50 eV), molybdenum hexafluoride (MoF_6, EA = 3.82 ± 0.19 eV), and rhenium hexafluoride (ReF_6, EA = $>5.14 \pm 0.48$ eV).[11] These results indicate that the electron binding energies of all five carborane anions are $>5.14 \pm 0.48$ eV. The value for $CHB_{11}Cl_{11}^-$ was further refined by obtaining its photoelectron spectrum at 157 nm at 70 K (Figure 2).[15] A broad band with a maximum at 7.0 eV was observed, and an adiabatic detachment energy (ADE) of 6.35 ± 0.02 eV was measured.[16] This is a remarkably large value for a nonsolvated, even-electron anion and is more than 1 eV greater than that for I^-, NO_3^-, $H_2PO_4^-$, FSO_3^-, HSO_4^-, $PhSO_3^-$, and ClO_4^- (EBE = 3.059036 ± 0.000044, 3.937 ± 0.014, 4.57 ± 0.01, 4.71 ± 0.19, and 4.75 ± 0.10, 5.0 ± 0.2, and 5.25 ± 0.1 eV, respectively).[11] It is well reproduced by B3LYP/6-311+G(d,p) and G3(MP2) calculations which give predicted electron affinities of 6.01 and 6.36 eV, respectively. This quantity provides another measure of the remarkable stability of carborane anions and is a direct consequence of σ aromaticity in the delocalized bonding of the CB_{11} cage.[17]

Direct equilibrium acidity determinations require a known reference acid within a few kcal mol^{-1} of the compound of interest. However, no such species is available for $H(CHB_{11}Cl_{11})$ so only an upper limit for ΔH°_{acid} is obtainable. On the other hand, the

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[†] University of Minnesota.
[‡] Washington State University and Pacific Northwest National Laboratory.
[§] University of California.
[ǁ] Current address: Department of Chemistry, Brown University, Providence, RI 02912.
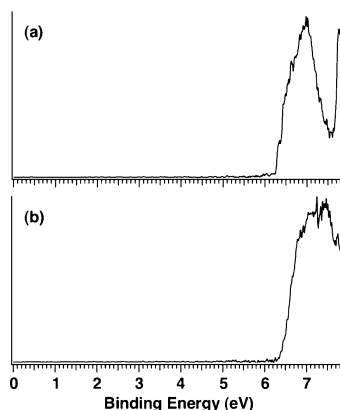
Figure 2. Photoelectron spectrum of $CHB_{11}Cl_{11}^-$ (a) and $(1\text{-}C_4F_9SO_2)_2N^-$ (b) at 157 nm (7.866 eV) at 70 K.

availability of the electron affinity of $CHB_{11}Cl_{11}^\bullet$ makes it possible to evaluate the thermodynamic cycle indicated by eq 1,

$$\Delta H^\circ_{\text{acid}}[H(CHB_{11}Cl_{11})] = BDE[H(CHB_{11}Cl_{11})] + IE(H^\bullet) - EA[CHB_{11}Cl_{11}^\bullet] \quad (1)$$

The ionization energy (IE) of a H atom (313.6 kcal mol^{-1}) is well-known. If the H−carborane bond dissociation energy (BDE) of the acid were known, then $\Delta H^\circ_{\text{acid}}[H(CHB_{11}Cl_{11})]$ would be directly available. While the BDE of the carborane acid is unknown, one can reasonably assume that the value is less than that for HCl (BDE < 103 kcal mol^{-1}) because the carborane radical is stabilized by delocalization.[11] A lower limit of 45 kcal mol^{-1} can be assigned by analogy to *tert*-butyl peroxide[18] and the observation that the carborane acid is thermally stable to at least 230 °C.[14] The resulting 45−103 kcal mol^{-1} range for the bond dissociation energy is consistent with the B3LYP/6-311+G(d,p) and G3(MP2) predictions of 62.5 and 70.0 kcal mol^{-1} and leads to a deprotonation enthalpy for the carborane acid between 212 and 270 kcal mol^{-1} (i.e., $\Delta H^\circ_{\text{acid}}[H(CHB_{11}Cl_{11})] = 241 \pm 29$ kcal mol^{-1}). Though imprecise, this value is in excellent accord with B3LYP/6-311+G(d,p) and G3(MP2) predictions of 237.6[5,8] and 238.3 kcal mol^{-1} and clearly indicates that $H(CHB_{11}Cl_{11})$ is the strongest gas-phase acid measured to date. It also bridges the gas-phase acidity and basicity scales for the first time.[19]

The record-breaking carborane deprotonation energy can be accounted for by the extremely high electron binding energy (stability) of its conjugate base, but is this the reason that carborane acids are such potent Brønsted acids? To address this question, the photoelectron spectrum of the $(1\text{-}C_4F_9SO_2)_2N^-$ anion was obtained (Figure 2). The spectrum is quite similar to that of $CHB_{11}Cl_{11}^-$ with a maximum at $\sim$7.3 eV and an ADE of 6.5 ± 0.1 eV.[15] These values are actually 0.2−0.3 eV larger than those for the carborane anion even though $H(CHB_{11}Cl_{11})$ is predicted to be 47.2 kcal mol^{-1} more acidic than $(1\text{-}C_4F_9SO_2)_2NH$ (i.e., 238.3 (G3(MP2)) − 291.1 (expt)). Clearly, the stability of the anions as reflected by their ADEs does not account for why the carborane acid is more acidic than the bis(nonafluorobutane-1-sulfonyl)imide although it plays a major role in the high acidity of these compounds. The difference in the

bond dissociation energies [BDE$(1\text{-}C_4F_9SO_2)_2$N−H = 127.4 $\pm$ 3.2 kcal mol^{-1} (expt., this work) vs BDE(H−$(CHB_{11}Cl_{11}))$ = 70.0 kcal mol^{-1} (G3(MP2))] is the key to the greater acidity of the carborane. To design even stronger Brønsted acids, one will need to balance both the stability of the anion and the BDE of the acid.

Supporting Information Available: Experimental details and computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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