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Oligomeric Carbocation-like Species from Protonation of Chloroalkanes

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S *Supporting Information*

ABSTRACT: The protonation of chloroethane by the strongest known solid superacid, the carborane acid $H(CHB_{11}Cl_{11})$, has been studied by quantitative IR spectroscopic methods to track mass balance and uncover previously unobserved chemistry. In the first step, an intermediate $EtCl \cdot H(CHB_{11}Cl_{11})$ species without full proton transfer to EtCl can be observed when d_5-deuterated chloroethane is used. It rapidly eliminates HCl (but not DCl) to form ethyl carborane, $Et(CHB_{11}Cl_{11})$, which binds a second molecule of chloroethane to form the Et_2Cl^+ chloronium ion. This undergoes a slower, previously unrecognized HCl elimination reaction to form a butyl carborane, $Bu(CHB_{11}Cl_{11})$, beginning an oligomerization process whereby unsymmetrical dialkylchloronium ions decompose to alkyl carboranes of formula $Bu(C_2H_4)_n(CHB_{11}Cl_{11})$ up to $n = 4$. Over time, a parallel competing process of de-oligomerization take place in the presence of free carborane acid that finishes with the formation of hexyl or butyl carboranes. Upon heating to 150 C, the final products are all converted to the remarkably stable *tert*-butyl cation carborane salt.

A lmost any molecule can be protonated by a superacid,[1,2] but protonated chloroalkanes have yet to be observed.[3,4] Rapid elimination of HCl from presumed $RClH^+$ ions and reaction with a second molecule of RCl results in the formation of dialkylchloronium ions (eq 1), which have recently been stabilized for X-ray structural studies as carborane anion salts.[5]

$$2RCl + H^+ \rightarrow [RClH]^+ + RCl \rightarrow R_2Cl^+ + HCl \qquad (1)$$

In pursuit of the elusive $[RClH]^+$ intermediate and in order to gain insight into the mechanism of R_2Cl^+ formation, we have studied the protonation of chloroethane on the surface of a carborane superacid. This was predicated on the idea that having the superacid in solid form and allowing it to interact with a chloroalkane in gaseous form would slow down the reaction and possibly allow us to observe intermediates. Indeed, a species related to the $[RClH]^+$ ion is detected when deuterated chloroethane is used, but to our surprise, oligomeric carbocation-like alkyl carboranes are also observed. This paper explores their origin and curious reactivity.

Chloroethane vapor was allowed to react anaerobically with a film of the "strong yet gentle" carborane acid, $H(CHB_{11}Cl_{11})$,[6] sublimed onto IR cell windows. Quantitative assessment of gaseous HCl release as a function of Et_2Cl^+ formation (Figure 1) revealed that the stoichiometry of eq 1 was not followed at any stage of the reaction.
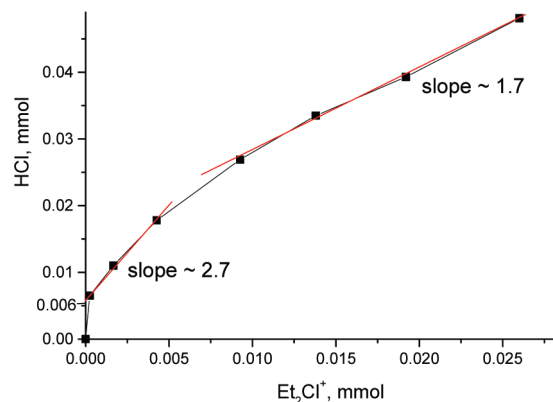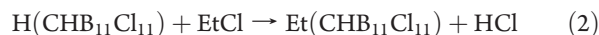

Figure 1. Dependence of released HCl on Et_2Cl^+ formation.

At the beginning of the reaction, HCl was released before significant Et_2Cl^+ was detected. This can be explained by early formation of the known[7] ethyl carborane (eq 2).

$$H(CHB_{11}Cl_{11}) + EtCl \rightarrow Et(CHB_{11}Cl_{11}) + HCl \qquad (2)$$

New ethyl group absorptions ascribable to the carbocation-like $Et(CHB_{11}Cl_{11})$ were detected in the IR spectrum of the solid phase after ca. 30 s. As shown in Table 1, the bands are similar to, but distinguishable from, those of EtCl and Et_2Cl^+.

Next, Et_2Cl^+ formation occurs according to eq 3, but never with the expected 1:1 overall stoichiometry of eqs 2 and 3, i.e., a slope of 1.0 in Figure 1.

$$Et(CHB_{11}Cl_{11}) + EtCl \rightarrow [Et_2Cl^+][CHB_{11}Cl_{11}] \qquad (3)$$
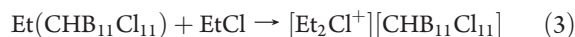
Instead, slopes considerably greater than 1.0 are observed throughout the reaction. Moreover, the overall mass balance of the completed room-temperature reaction (determined by lack of spectral change after 20 h, even after heating to 60 °C) did not correspond to a 1:1 ratio of HCl and Et_2Cl^+ ion. Rather, the ratio was 2:1.

The release of excess HCl can be explained by concomitant decomposition of Et_2Cl^+ to form butyl carborane (eq 4) on a time scale somewhat slower than its formation reaction.

$$[Et_2Cl^+][CHB_{111}Cl_{11}] \rightarrow Bu(CHB_{11}Cl_{11}) + HCl \qquad (4)$$

For the completed reaction, IR spectroscopy indicated that all the carborane acid had been consumed and that only $[Et_2Cl^+][CHB_{11}Cl_{11}^-]$ and $Bu(CHB_{11}Cl_{11})$ were present.

Table 1. Comparison of Ethyl Group IR Frequencies

assignment[a]	EtCl[b]	Et(CHB$_{11}$Cl$_{11}$)	Et$_2$Cl$^+$	d_{10}-Et$_2$Cl$^+$
$\nu_{as}CH_2$	3016 m	3057	3038 s	2287
$\nu_{as}CH_3$	3009 m	3006	3001 s	2256
$\nu_{as}CH_3$	2985 s	2990	2969 s	2242
$\nu_{s}CH_2$	2970 m	2976	2974 m	2184
$\nu_{s}CH_3$	2939 s	2952, 2933	2937 s	2115
$\delta_{as}CH_3$	1463 s	*	1447 m	1164
$\delta_{as}CH_3$	1455 m	1445	1436 s	1158
$\delta_{s}CH_3$	1381 s	1388	1381 s	1121
νCC	966 s	938	940 s	968

[a] In Ar matrix. See: Miller, F. A.; Kiviat, F. E. *Spectrochim. Acta* **1969**, *25A*, 1363. Dempster, A. B.; Zerby, G. *J. Mol. Spectrosc.* **1971**, *39*, 1. [b] Barnes, A. J.; Evance, M. L.; Hallam, H. E. *J. Mol. Struct.* **1983**, 235. *, overlapped with stronger bands from Et$_2$Cl$^+$.

Upon heating to 150 °C, these solids were transformed to a single product, the remarkably stable *tert*-butyl cation salt,[8] and the overall total molar amount of liberated HCl was exactly twice that of consumed acid. This indicates an overall stoichiometry as shown in eq 5.

$$H(CHB_{11}Cl_{11}) + 2EtCl \rightarrow [\textit{t-}Bu^+][CHB_{11}Cl_{11}{}^-] + 2HCl \quad (5)$$
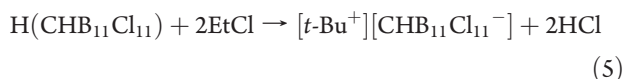
The conversion of *n*(or *i*)-Bu(CHB$_{11}$Cl$_{11}$) to the *tert*-butyl cation at elevated temperatures is readily understood in terms of 1,2 Meerwein shifts that are very rapid in "free" carbocations[9,10] but require heating when coordinated to carborane anions.

This tidy stoichiometry belies an underlying complexity of the reaction at intermediate stages of its progression. This is particularly apparent in experiments having lower vapor pressures of EtCl and is revealed by plotting released HCl versus consumed carborane acid rather than Et$_2$Cl$^+$ formation. For example, in an experiment at 39% lower EtCl pressure than that used in Figure 1, a plot of released HCl versus consumed acid, where contributions from eqs 2 and 3 have been subtracted, reveals substantial excess release of HCl that is not linearly correlated with acid consumption (Figure 2). The slope varies from ca. 8.35 to 1.55 over the 19.5 h reaction time.

These observations can only be explained by the formation of higher oligomeric alkyl carboranes according to eq 6, by analogy to eqs 3 and 4.

$$Bu(CHB_{11}Cl_{11}) + nEtCl \rightarrow Bu\text{-}(C_2H_2)_n\text{-}(CHB_{11}Cl_{11}) + nHCl \quad (6)$$
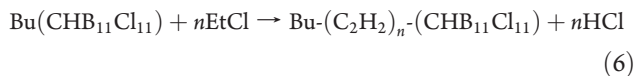
Precise mass balance calculations (see Supporting Information) indicate that *n* can reach average values upward of 4; i.e., there is formation of dodecanyl carborane, C$_{12}$H$_{23}$-(CHB$_{11}$Cl$_{11}$). Distinct R(CHB$_{11}$Cl$_{11}$) species cannot be identified by IR, and even their aggregate is difficult to quantify other than by mass balance calculations because of low IR molar intensities.

The formation of oligomeric R(carborane) compounds is reversible. After a maximum extent of oligomerization is reached, a de-oligomerization process sets in but never gets below Bu(carborane). Carborane acid replaces HCl in eq 6 as the acid required for the de-oligomerization process whose
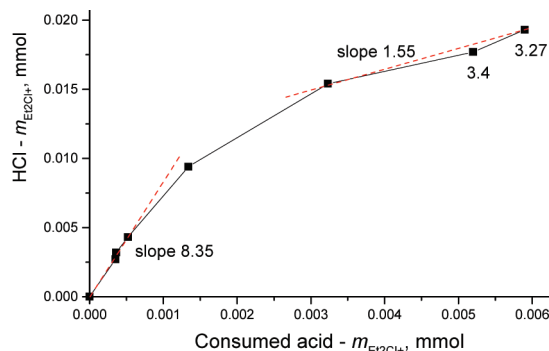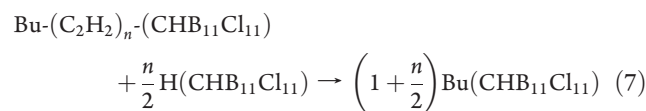

Figure 2. Dependence of HCl release on consumed carborane acid after deduction of contributions from eqs 2 and 3.

overall stoichiometry can be described by eq 7.

$$Bu\text{-}(C_2H_2)_n\text{-}(CHB_{11}Cl_{11})$$
$$+ \frac{n}{2} H(CHB_{11}Cl_{11}) \rightarrow \left(1 + \frac{n}{2}\right) Bu(CHB_{11}Cl_{11}) \quad (7)$$

Certain peculiarities are observed. In low EtCl pressure experiments, the de-oligomerization process stopped at hexyl rather than butyl carborane, and in these cases a strict 2:1 ratio of hexyl carborane to carborane acid was maintained throughout the entire process. Also curious is the observation that the final product of de-oligomerization, Bu(CHB$_{11}$Cl$_{11}$), does *not* interact with EtCl in the absence of free carborane acid. These results suggest an unusual chemical relationship between alkyl carboranes and the carborane acid.

In any case, the end point of all the solid phase reactions was a mixture of diethylchloronium ion salt together with Bu-(CHB$_{11}$Cl$_{11}$) or Bu(C$_2$H$_2$)(CHB$_{11}$Cl$_{11}$). If the mixture contained the latter (hexyl) carborane, then carborane acid was also present in a strict 2:1 ratio. All species are converted to *tert*-butyl cation at 150 °C with appropriate mass balance.

The reaction of the carborane acid with EtCl in the liquid phase proceeds in a similar manner to the gas/solid reaction. A mixture of H(CHB$_{11}$Cl$_{11}$) and EtCl evolves HCl gas and is rapidly converted to a precipitate of X-ray-characterized[5] chloronium ion salt [Et$_2$Cl$^+$][CHB$_{11}$Cl$_{11}{}^-$]. The supernatant retained the more soluble Bu(CHB$_{11}$Cl$_{11}$), and over time it evolved into oligomeric Bu-(C$_2$H$_4$)$_n$-CHB$_{11}$Cl$_{11}$.

Reaction rates are different with deuterated chloroethane, and the use of d_5-EtCl allowed us to see evidence for the long-sought intermediate of initial protonation. When d_5-EtCl was reacted with *protio*-H(CHB$_{11}$Cl$_{11}$), there was no label scrambling, and mass balance indicated a 17.5 mol % deficit of HCl. Although the IR spectrum of this "hidden" HCl-containing solid could not be separated with certainty from the intense spectrum of the chloronium ion, the *absence* of certain bands in the spectrum points to its structure. If proton transfer from the carborane acid to EtCl had occurred to produce an ion pair, [EtClH$^+$][CHB$_{11}$Cl$_{11}{}^-$], then a relatively narrow νClH$^+$ band from the EtClH$^+$ ion would be expected in the 2500−2800 cm^{-1} region. If the H(CHB$_{11}$Cl$_{11}$) acid simply formed a regular H-bond with EtCl, the easily detected νCCl band of chloroethane in the 600−650 cm^{-1} region would remain observable. However, neither region contained these bands. This result favors a structure with a more equally shared proton:

$$EtCl\text{-}\text{-}\text{-}H^+\text{-}\text{-}\text{-}Cl(CHB_{11}Cl_{10})^-$$
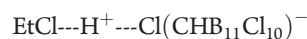
A very broad IR band from its ClH^+Cl group vibration would be expected in the $1500-2500$ cm^{-1} region. Its frequency would lie between those for the symmetric $[Cl-H-Cl]^-$ ion[11] and the asymmetric $[Cl-H-Br]^-$ ion whose H^+ is shifted somewhat toward the Cl atom.[12] Such a broad absorption is difficult to observe. Thus, the classical hydridochloronium ion, $EtClH^+$, does not exist with the carborane counterion because the basicities of EtCl and $CHB_{11}Cl_{11}{}^-$ are too similar.

In summary, the initial reaction of a carborane superacid with chloroethane involves a shared-proton intermediate that decays by HCl loss to form the carbocation-like ethyl carborane, Et-$(CHB_{11}Cl_{11})$. This reacts with EtCl to form the Et_2Cl^+ chloronium ion salt. Chloronium ions are unstable with respect to HCl loss and carbocation formation.

There is an intriguing relationship between these two classes of compounds that includes a facile oligomerization process up to $Bu(C_2H_2)_n(CHB_{11}Cl_{11})$ for $n = 4$ and a room-temperature de-oligomerization process that consumes carborane acid stoichiometrically, leading to $Bu(CHB_{11}Cl_{11})$ as the end product. All this has the potential to be manipulated in interesting ways in hydrocarbon processing and in chlorocarbon remediation whereby halocarbon solvent waste could be converted into hydrocarbon fuel. In future work we will extend these studies to homologues of chloroethane and to common polychlorinated solvents such as dichloromethane.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental details, IR spectra, and mass balance calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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