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Dialkyl Chloronium Ions

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Halonium ions (R_2X^+) are well-recognized reactive intermediates in electrophilic chemistry.[1,2] Because their stabilities increase down the halogen group, iodonium salts are commonly used reagents. Halonium ions in which R is a stabilizing aryl substituent have been isolated and structurally characterized for X = Cl, Br, I. With trialkylsilyl substituents, bridging fluorides with potential fluoronium ion character are also stable.[3] However, the existence of simple dialkylhalonium ions such as $(CH_3)_2X^+$ has only been determined spectroscopically, and the potential utility of the lighter element ions (e.g., X = Cl) as reagents is not well explored because they are stable only at low temperatures in synthetically challenging superacid media. Gas-phase dialkylhalonium ion chemistry has received more attention.[4] We now report that dimethyl- and diethylchloronium ions can be isolated from chloroalkane solvents at room temperature as carborane anion salts. This chemistry is enabled by the carborane acid $H(CHB_{11}Cl_{11})$, which matches the high acid strength needed to protonate chloroalkanes with a counterion that is exceptionally inert toward reactive cations and whose salts crystallize well.[5]

Colorless crystals of $CHB_{11}Cl_{11}^-$ salts of dimethyl- and diethylchloronium ions can be isolated in good yield by dissolution of anhydrous $H(CHB_{11}Cl_{11})$ in dry chloromethane and chloroethane, respectively, followed by partial solvent evaporation (eq 1):

$$2RCl + H(CHB_{11}Cl_{11}) \rightarrow [R_2Cl][CHB_{11}Cl_{11}](s) + HCl(g) \qquad (1)$$

The X-ray structures of the cations are shown in Figure 1.

The intrinsic symmetry of the dimethylchloronium ion is preserved crystallographically by location of the Cl atom on a twofold rotation axis. The C−Cl distance of 1.810(2) Å is somewhat shorter than the 1.855 Å value calculated using density functional theory (DFT) at the B3LYP/6-31G+(d,p) level.[6,7] The reverse trend might have been expected because of partial positive charge compensation by the anion in the crystal structure, suggesting that a higher level of theory may be needed to calculate the structure more accurately. The C−Cl distance is longer in the corresponding diethyl cation [1.840(6) Å], as expected for the larger cation on the basis of electrostatic arguments. The C−Cl−C angles are 101.5(1) and 105.8(2)°, respectively. These can be compared to the DFT-calculated value of 105.0° for the dimethyl cation.

The cation−anion interactions are consistent with an ionic solid having nearest atom−atom approaches close to the sum of the van der Waals radii. For example, the closest dimethylchloronium Cl to carborane Cl distance of 3.623 Å is slightly larger than the sum of the van der Waals radii[8] (3.5 Å). The closest CH···Cl interaction is 2.72 Å, compared with 2.86 Å for the sum of the van der Waals radii, but the C−H−Cl angle (136°) is too small for significant H bonding. In the diethyl salt, the closest cation−anion CH···Cl interaction occurs with the methylene group (H···Cl = 2.86 Å, C−H−Cl = 152°) rather than the methyl group (H···Cl = 2.93 Å, C−H−Cl = 166°), suggesting that delocalization of positive charge is attenuated with distance from the chloronium Cl atom.

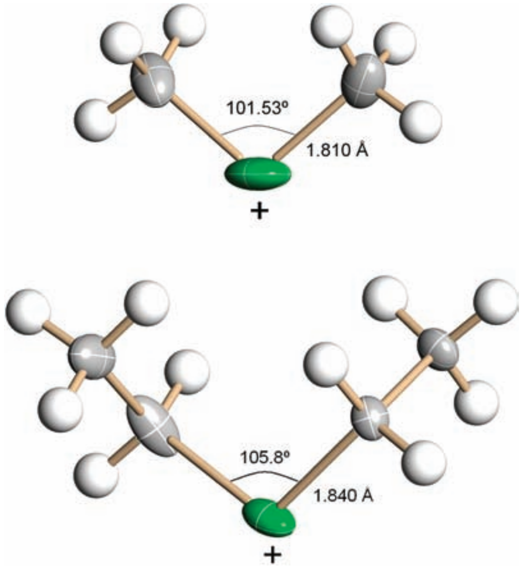

Figure 1. X-ray structures of (top) $(CH_3)_2Cl^+$ and (bottom) $(CH_3CH_2)_2Cl^+$ cations as $CHB_{11}Cl_{11}^-$ salts (Cl, green; C, gray; H, white).

Heating a sample of $[(CH_3)_2Cl][CHB_{11}Cl_{11}]$ to 140 °C in an IR cell under low pressure led to the observation of the spectrum of gaseous CH_3Cl (with rotational fine structure). Further heating to 160 °C under vacuum caused sublimation of $CH_3(CHB_{11}Cl_{11})$ onto the IR cell windows, indicating reaction according to eq 2:

$$[(CH_3)_2Cl][CHB_{11}Cl_{11}] \rightarrow CH_3(CHB_{11}Cl_{11}) + CH_3Cl \qquad (2)$$

This is an important method of isolating pure $CH_3(CHB_{11}Cl_{11})$, a potent electrophilic methylating agent that cannot be prepared using typical solution-phase chemistry because it reacts with all solvents, including hydrocarbons.[9,10] Reintroduction of gaseous CH_3Cl into the IR cell fully converted $CH_3(CHB_{11}Cl_{11})$ back to $[(CH_3)_2Cl][CHB_{11}Cl_{11}]$ within 30 s, indicating that eq 2 is reversible. Introduction of gaseous chloroethane to $CH_3(CHB_{11}Cl_{11})$ gave evidence for only the diethyl product and not the mixed methyl/ethylchloronium ion. This diethylchloronium ion salt does not sublime and has a more complex thermal decomposition.

The IR spectra of $[(CH_3)_2Cl][CHB_{11}Cl_{11}]$ and $CH_3(CHB_{11}Cl_{11})$ are shown in Figure 2, and frequency assignments are given in Table 1. The close similarity of the CH_3 group vibrations in CH_3Cl, $(CH_3)_2Cl^+$, and $CH_3(CHB_{11}Cl_{11})$ leads to confident assignments. To unambiguously identify the ν(CCl) frequency arising from the $H_3C{-}ClCHB_{11}Cl_{10}$ interaction, the spectrum of the deuterated methyl carborane $CD_3(CHB_{11}Cl_{11})$ was compared with that of the protio form. Their difference spectrum (Figure 3) removes absorptions from the $CHB_{11}Cl_{11}^-$ anion and sharply defines the ν(CCl) bands at 593 (protio) and 573 cm^{-1} (deutero) because they are

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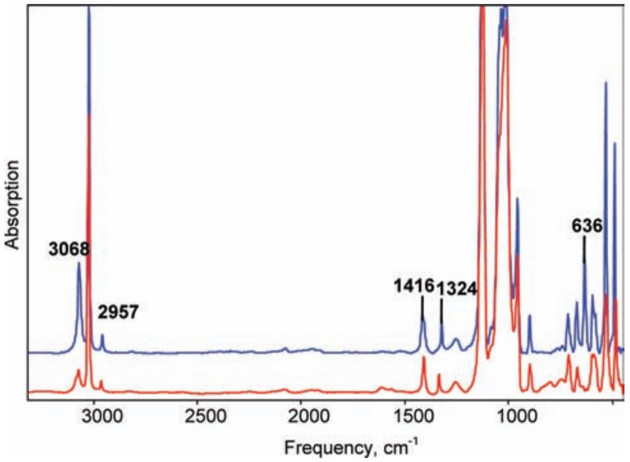

Figure 2. IR spectrum of $[(CH_3)_2Cl][CHB_{11}Cl_{11}]$ (blue, with labeled frequencies) compared with that of $CH_3(CHB_{11}Cl_{11})$ (red).

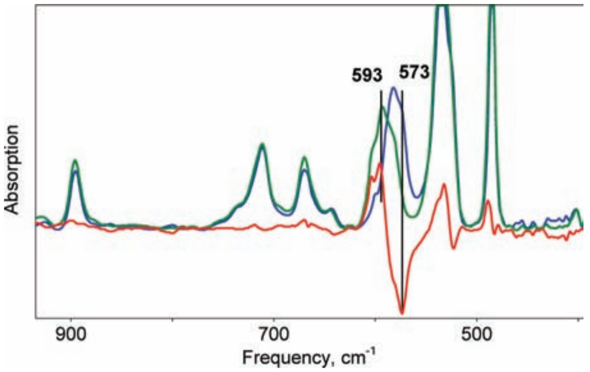

Figure 3. IR spectra of $CH_3[CHB_{11}Cl_{11}]$ (green) and $CD_3[CHB_{11}Cl_{11}]$ (blue). Their difference (red) reveals the ν(CCl) vibrations.

Table 1. Comparison of IR Frequencies of Methyl Species

assignment	$CH_3Cl(g)^a$	$(CH_3)_2Cl^+$	CH_3(anion)	CD_3(anion)	ν_H/ν_D
$\nu_{as}(CH_3)$	3042	3068	3084^b 3071^b	2321^b 2310^b	1.33 1.33
$\nu_s(CH_3)$	2966	2957	2962	2192	1.35
$\delta_{as}(HCH)$	1455	1416^b 1408^b	1409	1059	1.33
$\delta_s(HCH)$	1355	1324	1335	1009	1.32
$\delta_{as}(HCCl)$	1015	$-^c$	$-^c$	$-^c$	
ν(CCl A_1)	732	–	–	–	
ν[CCl(anion)]	–	–	593	573	1.04
$\nu_{as}(CClC)$	–	636	–	–	
$\nu_s(CClC)$	–	596	–	–	

[a] Data from ref 11. [b] Solid-state splitting of doubly degenerate band. [c] Weak band not identified.

slightly sensitive to H/D substitution. The IR spectrum of the $(CH_3)_2Cl^+$ ion is consistent with Raman spectra of dialkylhalonium ions collected in superacid media.[12]

The $\nu_{as}(CH_3)$ frequency increases by 26 cm^{-1} in going from CH_3Cl to $(CH_3)_2Cl^+$ and a further ~36 cm^{-1} in going to $CH_3(CHB_{11}Cl_{11})$ (Table 1). This indicates increasing positive charge on the CH_3 group and, consistent with the X-ray structure, indicates only a small role for CH•••Cl hydrogen bonding with the neighboring anions. Paralleling this trend, the νCCl frequencies decrease in the same sequence. This indicates decreasing C−Cl bond strength and increasing ionicity. Thus, $CH_3(CHB_{11}Cl_{11})$, which can be viewed as a neutral analogue of an asymmetric chloronium ion related to the dimethylchloronium ylide, CH_3ClCH_2,[7,13] has significantly greater CH_3^+ character and a longer H_3C-Cl bond. This greater ionic character is reflected in the relatively small perturbation of the IR spectrum of the carborane anion in $CH_3(CHB_{11}Cl_{11})$ relative to the free anion in $[(CH_3)_2Cl][CHB_{11}Cl_{11}]$ (1200−900 cm^{-1}). A higher degree of CH_3^+ character in $CH_3(CHB_{11}Cl_{11})$ explains its facile methylation of CH_3Cl to form the dimethylchloronium ion and its ability to abstract hydride from hydrocarbons at subambient temperatures, forming isolable carbocations.[9]

A comparison of the spectra of chloroethane and the diethylchloronium ion (see the Supporting Information) reveals that the trend of increasing ν(CH) applies to the methylene group but not to the methyl group. This indicates insignificant delocalization of positive charge beyond the CH_2 groups, as suggested by the X-ray data.

We tried to detect the presence of hydrochloronium ions, $RClH^+$, the expected intermediates in the protonation of chloroalkanes in eq 1. However, when RCl(g) was introduced into an evacuated IR cell containing a film of $H(CHB_{11}Cl_{11})$ sublimed onto its windows, only the spectra of gaseous HCl and dialkylchloronium ions were detected. The spectral transformation of solid $H(CHB_{11}Cl_{11})$ into solid $[R_2Cl][CHB_{11}Cl_{11}]$ showed distinct isosbestic points, excluding the detection of any intermediates. This indicates a low barrier to loss of HCl from hydrochloronium ions, $[RClH][CHB_{11}Cl_{11}]$.

The present findings reveal the relationship between dialkylchloronium ions and their more electrophilic charge-neutral analogues, $R(CHB_{11}Cl_{11})$. Similar to the manner in which diarylhalonium ions have been compared to C_2B_{10}-based carboranylhalonium ions,[14] this sets the stage for an exploration of their mechanisms of reactivity and their synthetic utility as isolable reagents.

Acknowledgment. This work was supported by NSF Grant CHE 0841428. We thank C. Knapp for a preprint of ref 10.

Supporting Information Available: Experimental details, IR spectra, and X-ray crystallographic data (CIF) for $[(CH_3)_2Cl]$-$[CHB_{11}Cl_{11}]$ and $[(CH_3CH_2)_2Cl][CHB_{11}Cl_{11}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA100297B