

# Preparation, NMR Spectroscopic, and *ab Initio*/DFT/GIAO-MP2 Studies of Halomethyl Cations<sup>1</sup>

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**Abstract:** A series of halomethyl cations was prepared and studied by <sup>13</sup>C NMR spectroscopy. Their structures and <sup>13</sup>C NMR chemical shifts were also calculated by *ab initio*/DFT/GIAO-MP2 methods. The  $\delta^{13}\text{C}$  of trihalomethyl cations  $\text{CX}_3^+$  (X = Cl, Br, I) and dimethylhalocarbenium ions  $\text{Me}_2\text{CX}^+$  (X = F, Cl, Br) correlate well with the Pauling electronegativities of the halogen atoms and  $\delta^{11}\text{B}$  of the isostructural and isoelectronic boron halides as well as with the calculated charge of carbon atoms. The  $\text{CF}_3^+$  cation was not observed, but a chemical shift of  $\delta^{13}\text{C}$  150 is indicated by comparison with other experimentally observed trihalomethyl cations. GIAO-MP2 chemical shift calculations gave  $\delta^{13}\text{C}$  169.2 for the  $\text{CF}_3^+$  cation.

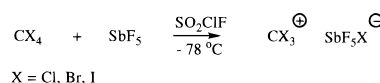
## Introduction

Several years ago in a preliminary communication,<sup>2</sup> we reported the preparation and <sup>13</sup>C NMR study of trihalomethyl cations. The trichloro, tribromo, and triiodomethyl cations were prepared by the ionization of their corresponding tetrahaloethanes in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solutions at low temperature as long lived ions (Scheme 1).

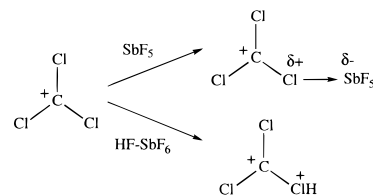
Halogen atoms adjacent to a carbocationic center are inductively destabilizing the cations due to their high electronegativity. However, halogen atoms in trihalomethyl cations  $\text{CX}_3^+$  can also stabilize the ions by the p–p interaction between the positively charged carbon atom and the nonbonded electrons pairs on the adjacent halogens accounting for the persistence of many alkylhalocarbenium ions under stable ion conditions.<sup>3</sup> The order of the charge-stabilizing effect of halogens on the thermodynamic stability of halomethyl cations was found to be  $\text{Cl} > \text{Br} > \text{I}$ . This order is in agreement with the relative increase in the size of the halogen atomic orbitals from chlorine to iodine leading to the least efficient overlap between positively charged carbon and iodine.<sup>4</sup>

The chemical reactivity of halomethyl cations in superacid media were studied by several groups. Sommer et al.<sup>5</sup> reported the increased reactivity of chloromethyl cations in hydride abstraction reactions with hydrocarbons in superacid media. They found that the reactivity decreased in the order  $\text{CCl}_3^+ > \text{CHCl}_2^+ \gg \text{CH}_2\text{Cl}^+$ . This was not expected because the stability of chloromethyl cations decreases in the same order since the number of 3p-electron donating chlorine atoms decreases. On these grounds  $\text{CCl}_3^+$  should be the least reactive species in the series. In order to explain this unusual behavior, protosolvation<sup>6</sup> of the chlorine atoms in superacid was suggested. If the halogen atoms of these ions were affected by further protolytic (or Lewis acid) interaction, the electron deficiency of the corresponding carbocationic centers would become more

## Scheme 1



## Scheme 2



pronounced, which should result in enhanced superelectrophilic reactivity (Scheme 2). Protosolvation should enhance the electrophilic character of carbon in the corresponding halomethyl ion leading to the higher reactivity in the hydride-abstraction. Therefore, as the number of halogen substituents increases, the electrophilicity should also augment. Similarly, the addition of  $\text{CCl}_4$  to the  $\text{HF-SbF}_5$  superacid system (and related superacids) as shown by Vančik et al.<sup>7</sup> also greatly enhanced their reactivity in hydride abstraction from hydrocarbons to form carbocations.

In related studies Vol'pin et al.<sup>8</sup> found that polyhalomethanes in the presence of excess of  $\text{AlBr}_3$  or  $\text{AlCl}_3$  exhibit the properties of aprotic superacids. For example,  $\text{CBr}_4 \cdot 2\text{AlBr}_3$ ,  $\text{CHBr}_3 \cdot 2\text{AlBr}_3$ ,  $\text{CCl}_4 \cdot 2\text{AlBr}_3$ , and  $\text{CHCl}_3 \cdot 2\text{AlBr}_3$  systems at 0–20 °C produce superelectrophiles which catalyze cracking, isomerization, and oligomerization of alkanes and cycloalkanes efficiently.

We now report in full our extended studies of halomethyl cations, including theoretical studies allowing a better understanding of their properties and reactivities.

## Results and Discussion

The  $\text{CCl}_3^+$  ion was prepared by slow addition of  $\text{CCl}_4$  to a solution of excess  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ . The <sup>13</sup>C NMR spectrum of the solution consists of a single sharp peak at  $\delta^{13}\text{C}$

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, April 1, 1996.

(1) Stable Carbocations, Part 299. For Part 298, see: Olah, G. A.; Buchholz, H. A.; Prakash, G. K. S.; Rasul, G.; Sosnowski, J. J.; Murray, R. K. Jr.; Kusnetsov, M. A.; Liang, S.; de Meijere, A. *Angew. Chem.* In press.

(2) Olah, G. A.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8020.

(3) *Carbocation Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley Interscience: New York, 1976; Vol. V, pp 2135–2262.

(4) Olah, G. A.; Mo, Y. K. In *Carbocation Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley Interscience: New York, 1976; Vol. V, Chapter 36.

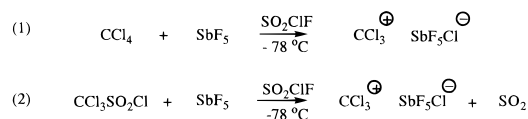
(5) Sommer, J.; Bukala, J. *Acc. Chem. Res.* **1993**, *26*, 370.

(6) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767. For a recent study, see: Olah, G. A.; Rasul, G.; Yudin, A. K.; Burrichter, A.; Prakash, G. K. S.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 1446.

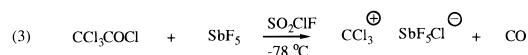
(7) Vančik, H.; Percac, K.; Sunko, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 7418.

(8) Vol'pin, M.; Akhrem, I.; Orlinkov, A. *New. J. Chem.* **1989**, *13*, 771.

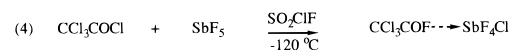
236.3. The same ion was also prepared by treating  $\text{CCl}_3\text{SO}_2\text{Cl}$  with  $\text{SbF}_5$  under identical conditions (reactions 1 and 2).



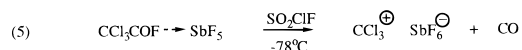
Similarly, when  $\text{CCl}_3\text{COCl}$  is subjected to superacidic ionizing reaction conditions, immediate evolution of carbon monoxide was observed; the  $^{13}\text{C}$  NMR, recorded at  $-78^\circ\text{C}$ , again shows a single peak at  $\delta^{13}\text{C}$  236.3 consistent with the formation of the  $\text{CCl}_3^+$  ion (reaction 3).



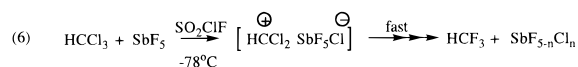
In order to trap the prospective intermediate trichloroacetyl cation,  $\text{CCl}_3\text{CO}^+$ , the experiment was repeated at  $-120^\circ\text{C}$ . At this temperature, the evolution of CO is sufficiently slowed down to observe a different set of  $^{13}\text{C}$  NMR signals, at  $\delta^{13}\text{C}$  92 and 194.8 ( $J_{\text{CF}} = 120$  Hz), caused by chloride-fluoride exchange at the acyl carbon, resulting in a donor-acceptor complex with a weakened C-F bond (reaction 4).



Upon warming this mixture to  $-78^\circ\text{C}$ , these resonances disappear and are replaced by a peak of  $\text{CCl}_3^+$  ion at  $\delta^{13}\text{C}$  236.3. We did not succeed in observing the expected resonance of the  $\text{CCl}_3\text{CO}^+$  cation (150–170 ppm) and conclude that the trichloroacetyl cation is not persistent under the used stable ion conditions. Its intermediate formation, however, must be invoked to account for the extrusion of CO and the subsequent appearance of the signal at  $\delta^{13}\text{C}$  236.3 characteristic of the  $\text{CCl}_3^+$  ion (reaction 5).



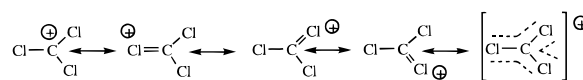
We also attempted to prepare the dichloromethyl cation by reacting chloroform  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$  (reaction 6). Chloroform does not give, however, a stable observable dichloromethyl cation,  $\text{HCCl}_2^+$ , but rather undergoes fast and complete fluorine-chlorine exchange since no other product other than trifluoromethane could be detected (reaction 6). This is, indeed, the equivalent of Swarts fluorination reaction. However, Vančik et al. were successful<sup>7</sup> in generating dichloromethyl cation in the solid  $\text{SbF}_5$  matrix at  $-123^\circ\text{C}$  and was characterized by IR spectroscopy.



Likewise, no persistent methyl ( $\text{CH}_3^+$ ) or chloromethyl cations ( $\text{H}_2\text{CCl}^+$ ), respectively, can be generated from methyl chloride or dichloromethane. Olah et al., however, reported<sup>9</sup> the preparation of bis(chloromethyl)chloronium ion  $\text{ClCH}_2\text{Cl}^+\text{CH}_2\text{Cl}$  by dissolving dichloromethane in a two-fold molar excess of  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  at  $-130^\circ\text{C}$ . Consequently, the intrinsic stability of  $\text{CCl}_3^+$  must stem from the ability of three chlorine atoms to symmetrically delocalize the positive charge from the cationic center (whereas the delocalization over two chlorine substituents seems not to be sufficient to observe the respective cation under long lived stable ion condition) (Scheme 3). This is in accord with the remarkably shielded cationic  $\delta^{13}\text{C}$  236.3 for  $\text{CCl}_3^+$ , compared to that in *tert*-butyl cation,  $\delta^{13}\text{C}$  336.

(9) Olah, G. A.; Bruce, M. R. *J. Am. Chem. Soc.* **1979**, *101*, 4765.

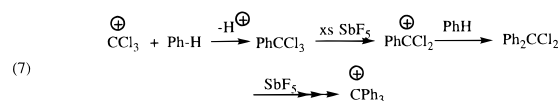
### Scheme 3



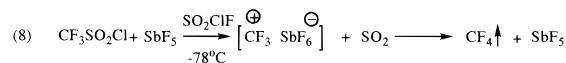
**Table 1.** Relative Stabilization Energies (SE) of Substituted Methyl Cations

ion	SE relative to $\text{CH}_3^+$ (kcal/mol)
$\text{CH}_3\text{OCH}_2^+$	66
$(\text{CH}_3\text{O})_2\text{CH}^+$	85
$(\text{CH}_3\text{O})_3\text{C}^+$	90
$\text{FCH}_2^+$	27
$\text{F}_2\text{CH}^+$	26
$\text{F}_3\text{C}^+$	14

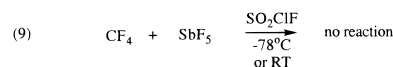
When benzene is added to the superacid solution of  $\text{CCl}_3^+$  a mixture of two carbenium ions is obtained, identified as triphenylmethyl and chlorodiphenylmethyl cations by  $^{13}\text{C}$  NMR spectroscopy, indicating the Friedel-Crafts type reaction sequence 7 of  $\text{CCl}_3^+$ .



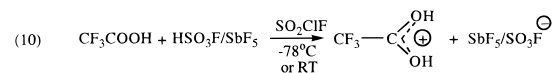
After the successful preparation and characterization of the trichloromethyl cation ion we attempted to obtain the trifluoromethyl cation,  $\text{CF}_3^+$ . When  $\text{CF}_3\text{SO}_2\text{Cl}$  was treated with  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ , only evolution of  $\text{CF}_4$  gas was observed, and no carbocationic resonance in the  $^{13}\text{C}$  NMR spectrum could be detected (reaction 8).



Similarly, the attempted ionization of  $\text{CF}_4$  with  $\text{SbF}_5$  neither at  $-78^\circ\text{C}$  in  $\text{SO}_2\text{ClF}$  nor in neat  $\text{SbF}_5$  even at room temperature resulted in any reaction 9.



Likewise, reaction of  $\text{CF}_3\text{COOH}$  with  $\text{HSO}_3\text{F}/\text{SbF}_5$  (1:1) (Magic Acid) only gave the protonated acid with no subsequent dehydration and decarbonylation at  $-78^\circ\text{C}$  or even at room temperature as evidenced by  $^{13}\text{C}$  NMR (reaction 10).



In our studies no  $\text{CF}_3^+$  was detected under any superacidic reaction conditions. In the gas phase, however,  $\text{CF}_3^+$  is readily observed as a high abundance fragment ion in the mass spectra of many organofluorine compounds.<sup>10</sup> Stabilization energies were calculated based on gas phase experiments<sup>11</sup> for methoxymethyl and fluoromethyl cations relative to  $\text{CH}_3^+$  which showed that  $\text{CF}_3^+$  is favored over  $\text{CH}_3^+$  by 14 kcal/mol (Table 1).

The order of stability of the fluoromethyl cations decreases with the increase in the substitution of fluorine for hydrogen. However, the trend in solution could be different when compared to the gas phase analogues (due to solvent effects, ion pairing, etc.). Thus, the existence of the well characterized<sup>12</sup>  $\text{CH}_3\text{CF}_2^+$  versus the elusive long lived  $\text{CH}_3\text{CH}_2^+$  cation in the

(10) Mohler, F. L.; Bloom, E. R.; Lengel, J. H.; Wise, L. G. *J. Am. Chem. Soc.* **1949**, *71*, 337.

(11) Martin, R. H.; Lange, F. W.; Taft, P. W. *J. Am. Chem. Soc.* **1966**, *88*, 1353.

(12) Olah, G. A.; Mo, Y. K. *J. Org. Chem.* **1972**, *37*, 1029.

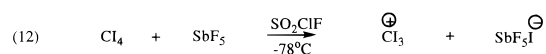
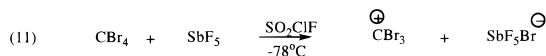
**Table 2.** Comparison of  $\delta^{13}\text{C}$  of Trihalomethyl Cations and Related Haloforms

X	H $\text{CX}_3$	$\text{CX}_3^+$	$\Delta\delta^{13}\text{C}$
Cl	77.7	236.3	158.6
Br	12.3 <sup>a</sup>	207	194.7
I	-139.7 <sup>a</sup>	95	234.7

<sup>a</sup> Reference 13.

condensed phase suggests that the replacement of hydrogen atoms by fluorine atoms provides stabilization for the carbocations. The reason for the elusiveness of the  $\text{CF}_3^+$  cation in solution is probably due to kinetic reasons wherein it is easily quenched with  $\text{F}^-$  ion to produce stable  $\text{CF}_4$ .

In contrast to  $\text{CF}_3^+$ ,  $\text{CBr}_3^+$  and  $\text{Cl}_3^+$  were obtained as persistent, stable ions when  $\text{CBr}_4$  and  $\text{Cl}_4$  were reacted with excess  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  and the  $^{13}\text{C}$  NMR spectra of the resulting ions were obtained (reactions 11 and 12).

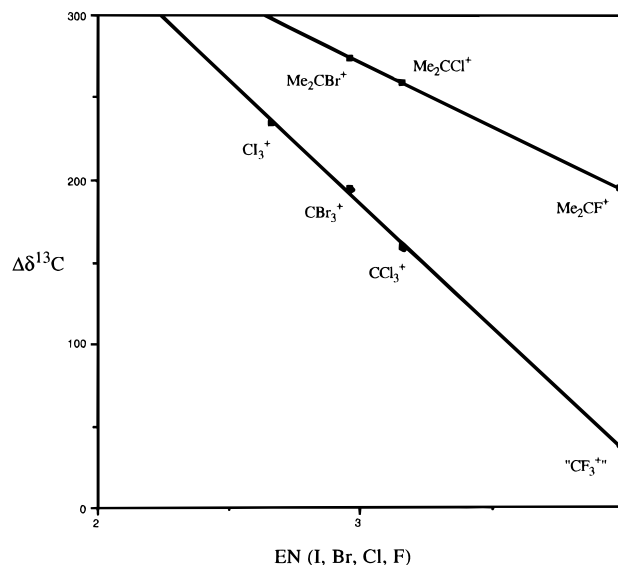


The  $^{13}\text{C}$  NMR spectra showed only single peaks at  $\delta^{13}\text{C}$  207 and 95, respectively, consistent with the formation of tribromomethyl and triiodomethyl cation. The  $\delta^{13}\text{C}$  95 of  $\text{Cl}_3^+$  represents the most shielded carbon chemical shift observed for a trivalent carbenium center under stable ion conditions. Bromine and iodine are known (based on their electronegativity) to have a less pronounced inductive electron withdrawing effect on adjacent  $\text{sp}^2$  carbon atoms than chlorine, but their ability to backdonate electron density into adjacent carbocationic centers is much diminished due to smaller degree of  $2\text{p}-4\text{p}$  and  $2\text{p}-5\text{p}$  overlap. Comparison of the differences in  $\delta^{13}\text{C}$  between  $\text{CCl}_3^+$ ,  $\text{CBr}_3^+$ , and  $\text{Cl}_3^+$  relative to the related haloforms  $\text{HCCl}_3$ ,  $\text{HCBBr}_3$ , and  $\text{HClI}_3$  reflects this trend (Table 2).

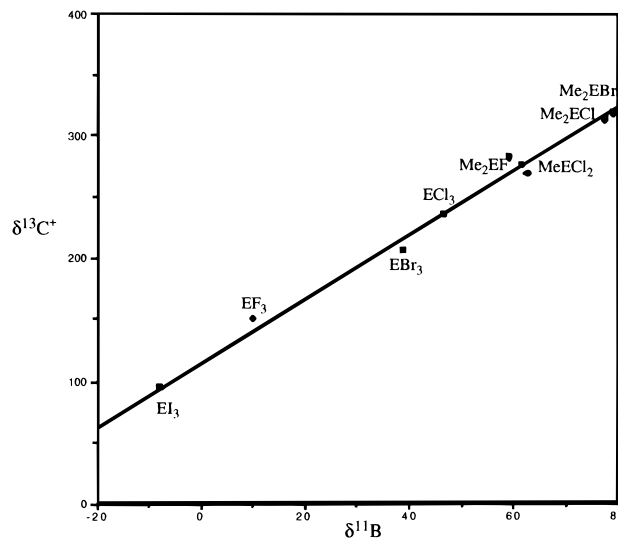
The chemical shift values are consistent with the decreasing order of backdonation  $\text{Cl} > \text{Br} > \text{I}$ . A plot of  $\Delta\delta^{13}\text{C}$  versus the Pauling electronegativity<sup>14</sup> of the respective halogens in  $\text{CX}_3^+$  results in a straight line. If this plot is extended to the electronegativity value of fluorine, the projected  $\delta^{13}\text{C}$  for the  $\text{CF}_3^+$  cation would be  $\delta^{13}\text{C}$  150.7 ( $\Delta\delta^{13}\text{C} = 37.2$  ppm). This implies that  $^{13}\text{C}$  shielding of fluorine correlates to its electronegativity similarly as it does for chlorine, bromine, and iodine. The validity of this hypothesis can be tested by plotting  $\Delta\delta^{13}\text{C}$  of the previously obtained<sup>3</sup> dimethylhalocarbenium ions,  $\text{Me}_2\text{CX}^+$  ( $\text{X} = \text{Br}, \text{Cl}, \text{F}$ ), against the electronegativity of X. Figure 1 shows both plots for  $\text{CX}_3^+$  and  $\text{Me}_2\text{CX}^+$ . The good correlation for  $\text{Me}_2\text{CX}^+$  cations confirms the validity of the suggestion. The slopes of the plots are  $-150.7$  and  $-78.4$  ppm/unit EN indicating diminished backbonding per halogen ligand upon increasing halogen substitution. In Table 3 we have listed  $\delta^{13}\text{C}$  of chloromethylcarbenium ions and their hydrogenated precursors.

To complete the study of the synergetic effect of stepwise halogen substitution in methyl cations,  $\delta^{13}\text{C}$  of dichloromethyl methyl cation was obtained to enable comparison with chlorodimethyl- and trichlorocarbenium ion (Table 3 and Figure 2).

Another approach of examining the validity of the electronegativity-shielding correlation in carbenium ions is provided by comparison of the calculated  $^{13}\text{C}$  chemical shifts with the  $^{11}\text{B}$  shifts of the analogous isoelectronic and isostructural boron compounds. Plotting the  $\delta^{11}\text{B}$  of  $\text{Me}_n\text{BX}_{3-n}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ )

(13) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 NMR Spectroscopy*; Wiley Interscience: New York, 1980.(14) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, 1939; p 58.**Figure 1.** Correlation of  $\Delta\delta^{13}\text{C}$  of halocarbenium ions with Pauling electronegativity.**Table 3.** Comparison of  $\delta^{13}\text{C}$  of Chloromethylcarbenium Ions and Their Hydroxo Analogues

	$\text{Me}_2\text{CCl}^+$	$\text{MeCCl}_2^+$	$\text{CCl}_3^+$
$\delta^{13}\text{C}$	313.8 <sup>a</sup>	276.0	236.3
$\delta^{13}\text{C}$ $\text{HCCl}_2$	54.9 <sup>a</sup>	69.2 <sup>b</sup>	77.7
$\Delta\delta^{13}\text{C}$	258.9	206.8	158.6

<sup>a</sup> Reference 3. <sup>b</sup> Reference 15.**Figure 2.** Correlation between  $\delta^{13}\text{C}$  and  $\delta^{11}\text{B}$  of halomethylcarbenium ions and methylboron halides.  $\delta^{13}\text{C}$  282.9 of  $\text{Me}_2\text{CF}^+$ ,  $\delta^{13}\text{C}$  313.8 of  $\text{Me}_2\text{CCl}^+$ , and  $\delta^{13}\text{C}$  319.8 of  $\text{Me}_2\text{CBr}^+$  of  $\text{C}^+$  of the ions were taken from ref 3.

versus the  $\delta^{13}\text{C}$  of the experimentally determined  $\text{Me}_n\text{CX}_{3-n}^+$  yields a good linear relationship (Figure 2).

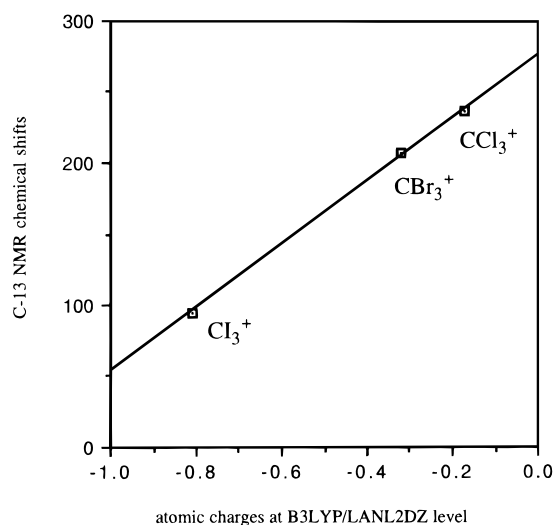
$\delta^{13}\text{C}$  for  $\text{CF}_3^+$  previously calculated from the electronegativity-shielding correlation (Figure 1) conform with the experimentally determined  $\delta^{11}\text{B}$  vs  $\delta^{13}\text{C}^+$  correlation line as seen in Figure 2, thus reinforcing the validity of such comparisons.

To study the charge distributions and its effect on  $^{13}\text{C}$  chemical shifts we have carried out<sup>16</sup> *ab initio* and density functional theory (DFT)<sup>17</sup> calculations on trihalomethyl cations at the MP2/LANL2DZ<sup>18</sup> and B3LYP<sup>19</sup>/LANL2DZ levels (as well as MP2/6-31G\* and B3LYP/6-31G\* for fluoro and chloro

(15) Stothers, J. B. *C-13 NMR Spectroscopy*; Academic Press: New York, 1972.

**Table 4.** Atomic Charges and Bond Lengths of Trihalomethyl Cations

ion	atomic charges		bond length	
	MP2/LANL2DZ (MP2/6-31G*)	B3LYP/LANL2DZ (B3LYP/6-31G*)	MP2/LANL2DZ (MP2/6-31G*)	B3LYP/LANL2DZ (B3LYP/6-31G*)
CF <sub>3</sub> <sup>+</sup>	C +1.12 (+1.30)	+0.77 (+0.97)	C–F 1.297 (1.246)	1.286 (1.244)
	F –0.04 (–0.10)	+0.07 (+0.01)		
CCl <sub>3</sub> <sup>+</sup>	C –0.02 (–0.17)	–0.17 (–0.25)	C–Cl 1.722 (1.648)	1.713 (1.663)
	Cl +0.34 (+0.39)	+0.39 (+0.42)		
CBr <sub>3</sub> <sup>+</sup>	C –0.29	–0.32	C–Br 1.885	1.879
	Br +0.43	+0.44		
CI <sub>3</sub> <sup>+</sup>	C –0.85	–0.81	C–I 2.067	2.065
	I +0.62	+0.60		

**Figure 3.** Plot of B3LYP/LANL2DZ atomic charges vs  $\delta^{13}\text{C}$  of carbon atoms of trihalomethyl cations.

compounds), respectively. All four trihalomethyl cations were optimized and the optimized bond lengths and Mulliken atomic charges are listed in Table 4.

At MP2/6-31G\* level CF<sub>3</sub><sup>+</sup> was found to have a C–F bond length of 1.246 Å which is 0.084 Å shorter (Table 4) than the C–F bond in CF<sub>4</sub>. This shortening is a result of efficient 2p–2p overlap between the nonbonded electron pairs on the fluorine atoms and adjacent positively charged carbon. The C–Cl bond length of 1.648 Å in CCl<sub>3</sub><sup>+</sup> is also significantly shorter compared to the C–Cl bond in CCl<sub>4</sub> (1.766 Å) indicating the positive charge in CCl<sub>3</sub><sup>+</sup> being delocalized among three chlorine atoms. Similar results are also found for CBr<sub>3</sub><sup>+</sup> and CI<sub>3</sub><sup>+</sup> ions (Table 4).

The B3LYP/LANL2DZ calculated Mulliken charge densities (Table 4) of carbon atom of trihalomethyl cations were plotted against the experimental  $\delta^{13}\text{C}$  (Figure 3). Observed good linear correlation (which may be fortuitous) indicates that for stable carbocations  $^{13}\text{C}$  chemical shifts can be directly correlated with the resident positive charge density on the cationic centers. However, the calculated charge density of carbon atom of the CF<sub>3</sub><sup>+</sup> ion does not closely reflect the predicted  $\delta^{13}\text{C}$ .

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We have also calculated the  $\delta^{13}\text{C}$  of CF<sub>3</sub><sup>+</sup> and CCl<sub>3</sub><sup>+</sup> ions at the correlated level of GIAO (Gauge Including Atomic Orbitals)-MP2<sup>20</sup> method using tzp<sup>20</sup> basis set on MP2/6-31G\* and B3LYP/6-31G\* geometries. At the GIAO-MP2/tzp//MP2/6-31G\* level the calculated  $\delta^{13}\text{C}$  of CF<sub>3</sub><sup>+</sup> is 169.2 ( $\delta^{13}\text{C}$  167.9 at the GIAO-MP2/tzp//B3LYP/6-31G\* level) and is close to the predicted value of 150.0 obtained from comparison with other known trihalomethyl carbocations. The calculated  $\delta^{13}\text{C}$  of CCl<sub>3</sub><sup>+</sup> is 249.9 ( $\delta^{13}\text{C}$  255.2 at the GIAO-MP2/tzp//B3LYP/6-31G\* level) compared with the experimental value of 236.0. At this time reliable  $^{13}\text{C}$  NMR chemical shift calculations of CBr<sub>3</sub><sup>+</sup> and CI<sub>3</sub><sup>+</sup> ions at the GIAO-MP2 method are not possible.

### Conclusions

Halomethyl cations were prepared under stable ion conditions and studied by  $^{13}\text{C}$  NMR spectroscopy. The structures and  $^{13}\text{C}$  NMR chemical shifts were also probed by *ab initio*/DFT/GIAO-MP2 methods. The  $^{13}\text{C}$  NMR chemical shifts of these cations are consistent with the decreasing order of backdonation Cl > Br > I. Furthermore, the  $^{13}\text{C}$  NMR chemical shifts of these ions correlate well with the Pauling electronegativities of the halogen atoms, the  $^{11}\text{B}$  NMR chemical shifts of the isostructural and isoelectronic boron halides, and also with the Mulliken charges of the carbon atoms. By comparison with the chemical shifts of other observed trihalomethyl cations  $\delta^{13}\text{C}$  of 150 was predicted for CF<sub>3</sub><sup>+</sup> cation, whereas the GIAO-MP2 calculated value is 169.2.

### Experimental Part

**NMR Spectroscopy.**  $^{13}\text{C}$  spectra were recorded on either a Varian Associates Model FT 80 (external lock) or Varian Associates Model VXR 200 (data system VXR 4000) NMR spectrometer equipped with a 10 and 5 mm broadband variable temperature probe, respectively. All  $^1\text{H}$  and  $^{19}\text{F}$  spectra were obtained on the latter, operating within an internal lock provided by an acetone-*d*<sub>6</sub> capillary.  $^1\text{H}$  and  $^{13}\text{C}$  resonances were referenced to external (capillary) tetramethylsilane,  $^{19}\text{F}$  signals to external CFCl<sub>3</sub> at  $\delta = 0.00$  ppm, respectively.

**Chemicals.** MeCCl<sub>3</sub>, CCl<sub>4</sub>, CCl<sub>3</sub>COCl, CCl<sub>3</sub>SO<sub>2</sub>Cl, CF<sub>4</sub>, CF<sub>3</sub>SO<sub>2</sub>Cl, CF<sub>3</sub>COOH, and CBr<sub>4</sub>, were commercially available (Aldrich, PCR) and used as received.

**Preparation of Halocarbenium Ions.** Freshly distilled SbF<sub>5</sub> was dissolved in approximately twice the volume of SO<sub>2</sub>ClF. To 1 mL of the solution in a test tube maintained at –78 °C (dry ice acetone bath) was slowly added, with vigorous stirring (vortex machine) and intermittent cooling, a precooled (–78 °C) solution of the precursor CX<sub>4</sub> (X = Cl, Br, I) in equal volume SO<sub>2</sub>ClF (total volume 0.3 mL). This solution (0.5 mL) was transferred into a 5 mm NMR tube under argon and kept at –78 °C. A cooled capillary tube (diameter 1.7 mm) containing the lock solvent acetone-*d*<sub>6</sub> was inserted fitted with Teflon spacers, and the NMR tube was transferred to the precooled variable temperature broadband probe (–60 °C) of the NMR spectrometer for spectroscopic studies. A sufficient signal to noise ratio was generally obtained after 500 transients for  $^{13}\text{C}$  and 10 transients for  $^{19}\text{F}$  spectra.

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