



In continuation of our work we now report density functional theory (DFT)<sup>14</sup> studies to investigate the electronic structure and properties of a series of methylhalonium ions and their protonated or methylated gtonic dications. Hydrogen/deuterium exchange experiment of dimethylbromonium ion, (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup>, in DF/SbF<sub>5</sub> superacid solution was also carried out. Besides activation of dimethylbromonium ion by bromine lone pair protonation, C–H protonation of the ion is also possible. C–H protonation of dimethylbromonium ion would lead to dication CH<sub>3</sub>Br<sup>+</sup>CH<sub>4</sub><sup>+</sup> involving a two-electron three-center (2e-3c) bond. Similar studies were also carried out on dimethylchloronium ion.

## Results and Discussion

Density functional theory (DFT) calculations were performed with the GAUSSIAN-94<sup>15</sup> package of programs. For X = F, Cl, and Br, the geometry and frequency calculations were performed at the B3LYP/6-31G\*\* level. Calculated energetics will be given at the B3LYP/6-31G\*\* + ZPE (at B3LYP/6-31G\*\* scaled by a factor of 0.96<sup>16</sup>) level, if not stated otherwise. For X = I, the geometry and frequency calculations were performed at the B3LYP/LANL2DZ (D95<sup>17</sup> on C and H, Los Alamos ECP plus DZ<sup>18</sup> on Br or I) level. Calculated energetics will be given at the B3LYP/LANL2DZ + ZPE (at B3LYP/LANL2DZ scaled by a factor of 0.96<sup>16</sup>) level, if not stated otherwise. The total energies of the calculated structures are shown in (Tables 1 and 2). Atomic charges and Löwdin<sup>19</sup> bond order were obtained using the natural bond orbital analysis (NBO)<sup>20</sup> method (Figures 1 and 2).

**H<sub>3</sub>X<sup>2+</sup> (X = F, Cl, Br, I):** DFT calculated structures of H<sub>3</sub>X<sup>2+</sup> as well as H<sub>2</sub>X<sup>+</sup> agree well with the recently reported ab initio MP2(FU)/6-31G\*\* structures of Boldyrev and Simons.<sup>7</sup> C<sub>3v</sub> symmetrical dications H<sub>3</sub>Cl<sup>2+</sup> **2b**, H<sub>3</sub>Br<sup>2+</sup> **2c**, and H<sub>3</sub>I<sup>2+</sup> **2d** were found to have considerable, 27.4, 37.9, and 35.8 kcal/mol, kinetic barriers for deprotonation through transition structures **3b**, **3c**, and **3d**, respectively, although their dissociation into H<sub>2</sub>X<sup>+</sup> and H<sup>+</sup> is exothermic by 66.9, 44.4, and 35.0 kcal/mol. On the other hand H<sub>3</sub>F<sup>2+</sup> **2a** has a planar D<sub>3h</sub> structure and has only 8.6 kcal/mol dissociation barrier. Trication **2a** is also thermodynamically highly unstable toward dissociation into H<sub>2</sub>F<sup>+</sup> **1a** and H<sup>+</sup> by 106.4 kcal/mol. Löwdin bond orders of X–H bond of the trications **2a**, **2b**, **2c**, and **2d** are 0.67, 0.87, 0.88, and 0.95, respectively, and the atomic charges of X of the trications are –0.51, 0.38, 0.67, and 1.19. These results are consistent with the order of the electronegativities (F > Cl > Br > I) and also the order of the size (I > Br > Cl > F) of the

**Table 1.** Energies (–au), ZPE<sup>a</sup>, Relative Energies,<sup>b</sup> and Proton Affinity

ions	B3LYP/6-31G**	ZPE	rel energy	proton affinity
Fluoro				
<b>1a</b>	100.63698	11.5	0.0	–104.9
<b>2a</b>	100.47049	13.4	106.4	
<b>3a</b>	100.45386	11.6	115.0	
<b>4a</b>	139.98389	29.5	0.0	–48.0
<b>5a</b>	139.90879	31.9	49.5	
<b>6a</b>	179.31610	47.2		
<b>9a</b>	218.67481	66.9		
Chloro				
<b>1b</b>	461.01824	9.2	0.0	–65.4
<b>2b</b>	460.91866	13.6	66.9	
<b>3b</b>	460.86928	10.0	94.3	
<b>4b</b>	500.36397	27.8	0.0	–27.3
<b>5b</b>	500.32063	29.4	28.8	
<b>6b</b>	539.70292	46.1	0.0	–9.2
<b>8b</b>	539.68891	48.0	10.7	
<b>9b</b>	579.07919	67.1		
Bromo				
<b>1c</b>	2572.54083	8.3	0.0	–42.9
<b>2c</b>	2572.47744	12.9	44.4	
<b>3c</b>	2572.41091	9.1	82.3	
<b>4c</b>	2611.88736	26.9	0.0	–18.7
<b>5c</b>	2611.85709	28.1	20.2	
<b>6c</b>	2651.22766	45.4	0.0	18.9
<b>7c</b>	2651.26064	48.7	–17.4	
<b>8c</b>	2651.22407	47.4	4.3	
<b>9c</b>	2690.62733	67.0		

<sup>a</sup> Zero point vibrational energies (ZPE) in kcal/mol at B3LYP/6-31G\* level scaled by a factor of 0.96. <sup>b</sup> Relative energies based on B3LYP/6-31G\* // B3LYP/6-31G\* + ZPE.

**Table 2.** Energies (–au), ZPE<sup>a</sup>, Relative Energies,<sup>b</sup> and Proton Affinity

ions	B3LYP/LANL2DZ	ZPE	rel energy	proton affinity
Iodo				
<b>1d</b>	12.20203	7.2	0.0	–33.5
<b>2d</b>	12.15332	11.6	35.0	
<b>3d</b>	12.09005	7.7	70.8	
<b>4d</b>	51.54549	26.3	0.0	–11.5
<b>5d</b>	51.52910	29.0	13.0	
<b>6d</b>	90.88292	45.1	0.0	19.5
<b>7d</b>	90.91618	48.0	–18.0	
<b>8d</b>	90.88792	47.2	–1.0	
<b>9d</b>	130.27660	66.7		

<sup>a</sup> Zero point vibrational energies (ZPE) in kcal/mol at B3LYP/LANL2DZ level scaled by a factor of 0.96. <sup>b</sup> Relative energies based on B3LYP/LANL2DZ // B3LYP/LANL2DZ + ZPE.

halogen atoms.<sup>2</sup> The electronegativities and size of the halogens atoms are also in line with the calculated proton affinities of the H<sub>2</sub>X<sup>+</sup> ions (X = F –104.9, Cl –65.4, Br –42.9, I –33.5).

As mentioned, the greatly increased reactivity<sup>6</sup> of the HF–SbF<sub>5</sub> superacid-catalyzed carbonylation of alkanes upon adding Br<sup>–</sup> ion could be due to protolytic activation of H<sub>2</sub>Br<sup>+</sup> to gtonic H<sub>3</sub>Br<sup>2+</sup>.<sup>5</sup> Thermodynamically the H<sub>3</sub>Br<sup>2+</sup> dication is expected to be more stable in the solution than in the gas phase. Olah et al. reported<sup>5</sup> experimental and theoretical studies of the H<sub>4</sub>O<sup>2+</sup> dication. In fact hydrogen–deuterium exchange experiments of isotopomeric H<sub>3</sub>O<sup>+</sup> in superacids were found to indicate more rapid exchange upon increase of acidity of the media. This exchange was suggested to proceed via an associative mechanism involving H<sub>4</sub>O<sup>2+</sup> dications. In comparison, the calculated proton affinity (PA) of H<sub>2</sub>Br<sup>+</sup> (–42.9 kcal/mol) is even more than PA of H<sub>3</sub>O<sup>+</sup> (–60.4 kcal/mol). On the other hand the calculated dissociation barrier of H<sub>3</sub>Br<sup>2+</sup> (37.9 kcal/mol) is very close to the dissociation barrier of H<sub>4</sub>O<sup>2+</sup> (38.2 kcal/mol).

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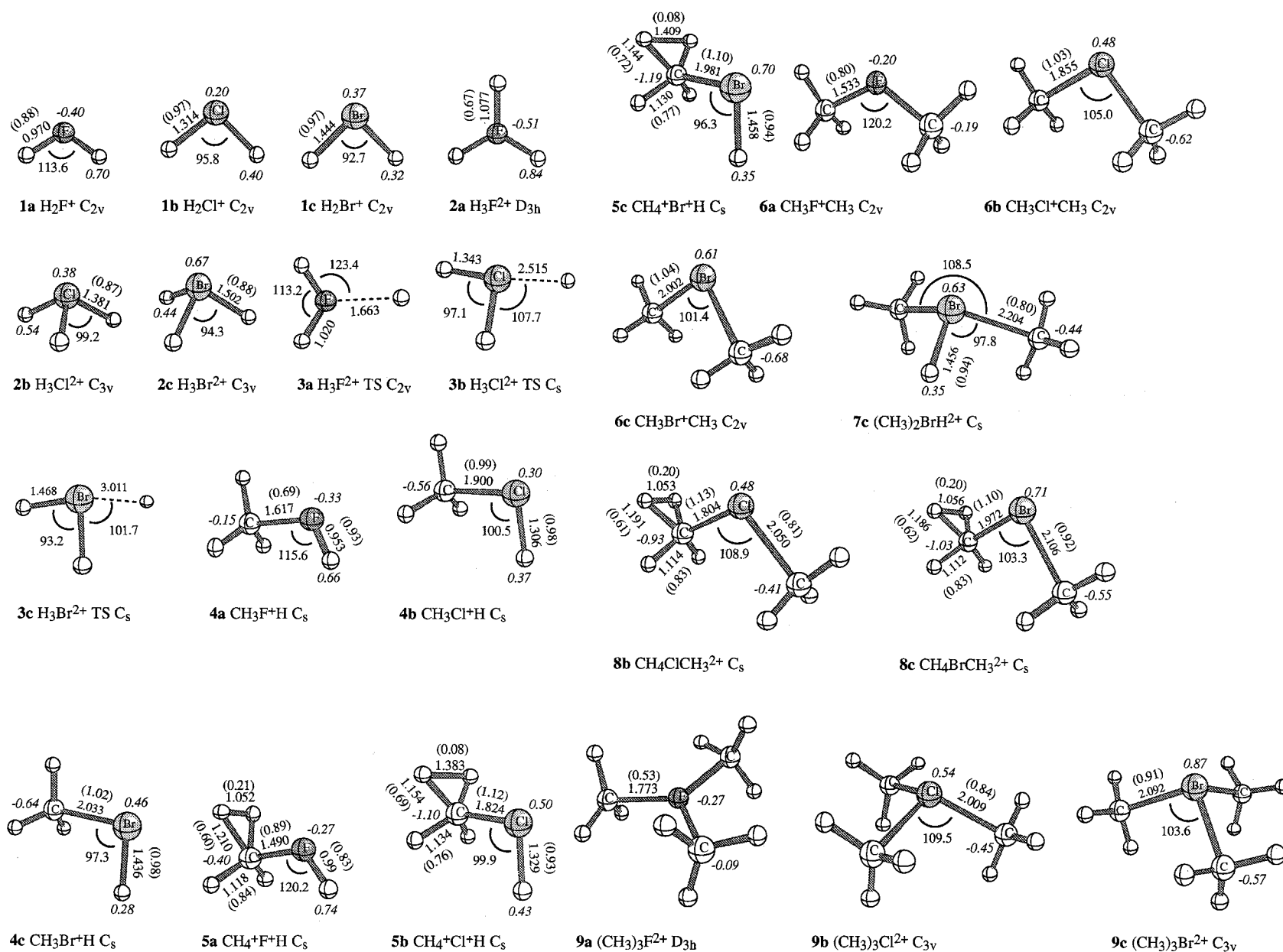
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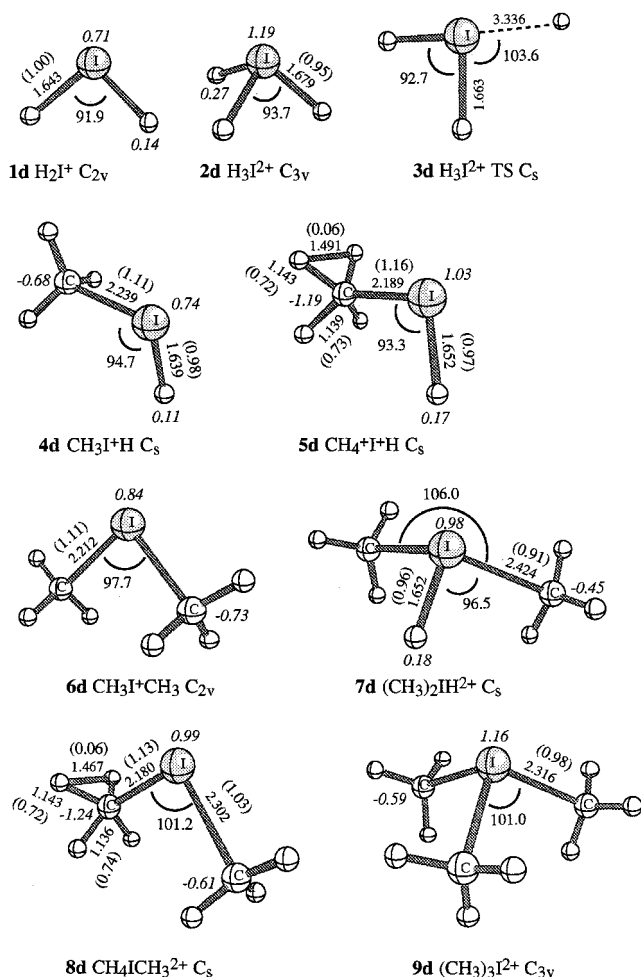
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**Figure 1.** B3LYP/6-31G\* calculated selected parameters, NBO charges (in italics), and Lowdin bond orders (in parentheses).



**Figure 2.** B3LYP/LANL2DZ calculated selected parameters, NBO charges (in italics), and Lowdin bond orders (in parentheses).

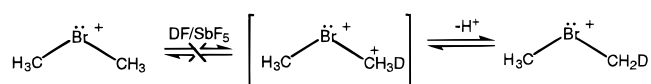
**CH<sub>4</sub>XH<sup>2+</sup>** (X = F, Cl, Br, I): Second protonation of protonated methyl halides (**4a–d**) seem to occur primarily on the C–H bonds, since the B3LYP/6-31G\*\* potential energy surfaces (PES) for CH<sub>3</sub>XH<sub>2</sub><sup>2+</sup> were found to be repulsive. Each of the C–H protonated structure **5a–d** contains a pentacoordinate carbon with a 2e-3c bond. The involvement of 2e-3c bonding in these dications is clearly indicated from their calculated structures and bond orders (BO). However, the nature of 2e-3c bonding is significantly different from one dication to another (e.g., the BO of 2e-3c H–H bond in fluoronium ion **5a** is 0.21, and that of iodonium ion **5d** is only 0.06). Expectedly the halogen atoms carry significantly more charge in dications than in their corresponding monocations. Thermodynamically the dications **5a**, **5b**, **5c**, and **5d** are 49.5, 28.8, 20.2, and 13.0 kcal/mol, respectively, less stable than their corresponding parent monocations (Table 1 and 2).

**(CH<sub>3</sub>)<sub>2</sub>XH<sup>2+</sup>** and **CH<sub>3</sub>X+H(CH<sub>4</sub><sup>+</sup>)** (X = F, Cl, Br, I): Dimethylhalonium ions can also undergo protonation either on halogen atom or on carbon atom. However, neither of the F– or C–H protonated dimethylfluoronium dication corresponds to a minimum. Whereas Cl-protonated dimethylchloronium dication is not a minimum, C–H protonated dimethylchloronium dication **8b** does correspond to a minimum. The dication **8b** contains a pentacoordinate carbon with a 2e-3c bond. Thus, the structure **8b** is in fact a chloronium–carbonium dication. Thermodynamically **8b** is only 10.7 kcal/mol less stable than the monocation, dimethylchloronium ion **6b**. The proton affinity

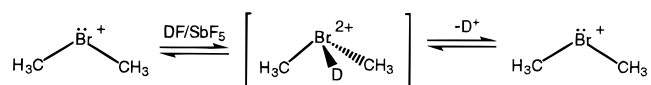
of dimethylchloronium ion **6b** was calculated to be –9.2 kcal/mol.

On the other hand, both Br<sup>–</sup> and C–H protonated dimethylbromonium dications **7c** and **8c**, respectively, were found to be minima. The structure **7c** is 21.7 kcal/mol more stable than the structure **8c**. The structure **8c** involves a 2e-3c bond and can be considered as bromonium–carbonium dication. The 18.9 kcal/mol proton affinity of dimethylbromonium ion **6c** suggests that the formation of dication **7c** in the gas phase is an exothermic process. Similar to bromine analogues, each of the I– and C–H protonated dimethyliodonium dication **7d** and **8d**, respectively, correspond to a energy-minimum. The I-protonated form **7d** is 19.0 kcal/mol more stable than the C–H protonated form **8d**. Similar to bromine analogue **8c**, the C–H protonated dimethyliodonium dication **8d** also possesses a 2e-3c bond. The dication **7d** is 18.0 kcal/mol more stable than the dimethyliodonium ion **6d**.

**Hydrogen–Deuterium Exchange Study on Dimethylbromonium and Dimethylchloronium Ions.** Dimethylbromonium ion, (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup>, was prepared by reacting excess methyl bromide with SbF<sub>5</sub> in SO<sub>2</sub> at –78 °C and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup>SbF<sub>6</sub><sup>–</sup> salt was isolated from the solution by evaporating SO<sub>2</sub>. Dimethylbromonium ion was treated with excess of 4:1 DF/SbF<sub>5</sub> superacid at –78 °C and was allowed to slowly warm to –20 °C. The 4:1 DF/SbF<sub>5</sub> is one of the strongest superacid systems known.<sup>3</sup> The resulting solution was periodically monitored by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy to observe any hydrogen/deuterium exchange at the CH<sub>3</sub> groups of (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup>. Under these conditions and over a period of 15 days, no exchange could be detected. Even at room temperature no exchange products or decomposition of the (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup> ion was detected by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy over a period of about 1 day (within the detection limit of NMR; ≤0.5%). To account for the absence of isotopic exchange, protonation (deuteration) of the (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup> ion at the methyl group can be excluded.



The enhanced reactivity of dimethylbromonium ion under superacid conditions,<sup>5</sup> therefore, must be due to the formation of the superelectrophilic, gitonic Br-protonated dimethylbromonium dication (CH<sub>3</sub>)<sub>2</sub>BrH<sup>2+</sup> as the de facto reactive intermediate and not the C–H protonated CH<sub>3</sub>Br<sup>+</sup>CH<sub>4</sub><sup>+</sup>. Thus, the observed lack of hydrogen/deuterium exchange in the present study is in accord with the calculations which show that the Br-protonated form **7c** is 21.7 kcal/mol more stable than the C–H protonated form **8c**.



Dimethylchloronium ion, (CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup>, was also treated with excess of 4:1 DF/SbF<sub>5</sub> superacid at –78 °C and was allowed to slowly warm to –20 °C. Under these conditions and over a period of 15 days, no exchange could be detected at the CH<sub>3</sub> groups of (CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup>. Similar to (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup> ion, even at –10 °C no exchange products or decomposition of the (CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> ion was detected over a period of about 4 days. These results suggest that dimethylchloronium ion might not undergo protonation under these conditions since our calculations indicate that



any C–H or Cl protonation should give exchange products or decomposition.

Similar hydrogen/deuterium exchange was also not observed at the CH<sub>3</sub> groups of the long-lived trimethyloxonium ion, (CH<sub>3</sub>)<sub>3</sub>O<sup>+</sup>, when treated with excess DF/SbF<sub>5</sub> superacid.<sup>21</sup> The lack of hydrogen/deuterium exchange in (CH<sub>3</sub>)<sub>3</sub>O<sup>+</sup> is also consistent with theoretical calculations which showed that the O-protonated trimethyloxonium dication (CH<sub>3</sub>)<sub>3</sub>OH<sup>2+</sup> is more stable than the C–H protonated (CH<sub>3</sub>)<sub>2</sub>O<sup>+</sup>CH<sub>4</sub><sup>+</sup> by 31.2 kcal/mol.<sup>21</sup> Acetyl cation also showed similar behavior with O-protonation preferred over C–H protonation in DF/SbF<sub>5</sub> medium. Previously, we have been able to show by hydrogen/deuterium exchange experiments and theoretical calculations that long-lived stable alkyl cations, such as *tert*-butyl<sup>22</sup> and 2-propyl cations,<sup>23</sup> can undergo C–H protonation to form highly electron deficient *protio*-alkyl dications.

(CH<sub>3</sub>)<sub>3</sub>X<sup>2+</sup> (X = F, Cl, Br, I): We also calculated the structures of methylated dimethylhalonium dications. The C<sub>3v</sub> symmetrical (CH<sub>3</sub>)<sub>3</sub>Cl<sup>2+</sup> **9b**, (CH<sub>3</sub>)<sub>3</sub>Br<sup>2+</sup> **9c**, and (CH<sub>3</sub>)<sub>3</sub>I<sup>2+</sup> **9d** were found to be the stable minima. The fluoro analogue (CH<sub>3</sub>)<sub>3</sub>F<sup>2+</sup> **9a** is also a minimum but has a planar D<sub>3h</sub> structure with a relatively long C–F bond. Lowdin bond orders of X–C bond of the trications **9a**, **9b**, **9c**, and **9d** are 0.53, 0.84, 0.91, and 0.98, respectively, indicating a very weak C–F bond in **9a** compared to other halonium dications. The order of increasing atomic charges of halogen atom of the dications (*F* = –0.27, Cl = 0.54, Br = 0.87, and I = 1.16) again corresponds to the order of the electronegativities (F > Cl > Br > I) as well as the order of the sizes (I > Br > Cl > F) of the halogens atoms.

Our present studies support that the increased reactivity of dialkylhalonium ions in superacid solutions is due to the protolytic (or electrophilic) activation involving probably the nonbonded electron pair of the halogen atoms leading to dicationic superelectrophiles.<sup>5</sup> We previously reported<sup>24,25</sup> that superelectrophilic activation offers an adequate explanation of the observed experimental data for a variety of superacid-

catalyzed reactions. Herein we have applied the principle to the dimethylhalonium ions. If the halogen atoms of these ions are further protonated, the electron deficiency of the systems would become more pronounced resulting in enhanced reactivity.<sup>5</sup>

## Conclusions

Structures and energies of a series of diprotonated hydrogen halides (H<sub>3</sub>X<sup>2+</sup>) and gtonic protio methyl- and dimethylhalonium dications (CH<sub>3</sub>XH<sub>2</sub><sup>2+</sup> and (CH<sub>3</sub>)<sub>2</sub>XH<sup>2+</sup>) were calculated using DFT B3LYP/6-31G\*\* level of theory. Proton affinities and thermodynamics of the dications were also calculated. Hydrogen/deuterium exchange experiments were carried out on the dimethylbromonium ion, (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup> (as well as on the dimethylchloronium ion, (CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> ion), by reacting (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup> SbF<sub>6</sub><sup>–</sup> with excess 4:1 DF/SbF<sub>5</sub> superacid at –20 °C as well as room temperature. No exchange was observed at the CH<sub>3</sub> groups of (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup> or (CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> which would involve the intermediacy of the corresponding Br,C-protio (deuterio) dimethylbromonium dications. The lack of hydrogen/deuterium exchange was discussed by using calculated data.

## Experimental Section

Methyl bromide (Aldrich), methyl chloride, anhydrous HF (Setic Lab), D<sub>2</sub>O (Acros), and benzoyl chloride (Lancaster) are commercially available products and were used as received. Antimony pentafluoride (Allied-Chemical) was doubly distilled prior to use. DF was prepared by reacting benzoyl fluoride and D<sub>2</sub>O.<sup>26</sup> Benzoyl fluoride was prepared from benzoyl chloride and anhydrous HF as previously reported.<sup>27</sup>

<sup>1</sup>H and <sup>2</sup>H NMR spectra were obtained on a Varian 300 spectrometer equipped with a variable temperature probe at 300 and 46.0 MHz, respectively. Five millimeter Quartz NMR tubes were used for samples containing DF. NMR spectra were referenced using an acetone-*d*<sub>6</sub> capillary as the external standard.

**H/D Exchange Experiments with DF/SbF<sub>5</sub>.** (CH<sub>3</sub>)<sub>2</sub>Br<sup>+</sup> SbF<sub>6</sub><sup>–</sup> or (CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> SbF<sub>6</sub><sup>–</sup> (ca. 150 mg) was placed in a Kel-F tube and cooled to –78 °C in a dry ice/acetone bath. Approximately 2 mL of DF/SbF<sub>5</sub> (4:1 molar solution) was added at –78 °C. The ensuing mixture was vigorously stirred and (Vortex stirrer) was kept at –20 °C and periodically monitored by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy.

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