Diprotonated Hydrogen Halides (H_3X^{2+}) and Gitonic Protio Methyland Dimethylhalonium Dications $(CH_3XH_2^{2+})$ and $(CH_3)_2XH^{2+}$: Theoretical and Hydrogen–Deuterium Exchange Studies¹

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Abstract: Density functional theory (DFT) calculations at the B3LYP/6-31G** level were performed to investigate geometries and energies of a series of diprotonated hydrogen halides (H_3X^{2+}) and gitonic protio methyl- and dimethylhalonium dications $(CH_3XH_2^{2+} \text{ and } (CH_3)_2XH^{2+})$. On the basis of computed energies, proton affinities and related thermodynamic parameters were also calculated. A hydrogen/deuterium exchange experiment of dimethylbromonium ion, $(CH_3)_2Br^+$, with an excess of 4:1 DF/SbF₅ superacid indicated lack of exchange at the methyl group supporting protonation of the nonbonded electron pair on the bromine leading to the involvement of gitonic protodimethylbromonium dication. A similar hydrogen/deuterium exchange experiment was also carried out on dimethylchloronium ion, $(CH_3)_2Cl^+$.

Introduction

Halonium ions are an important class of onium ions.² Their role as reaction intermediates (in halogenation, Friedel–Crafts alkylation reaction, etc.) and in preparative chemistry is well recognized.² Dialkyl (aryl) halonium ions are closely related to the alkyloxonium ions (Meerwein salts) but offer better selectivity. Dialkyl chloro-, bromo-, and iodohalonium ions can be prepared as stable long-lived ions.^{2–4} However, no stable dialkylfluoronium ion has been obtained in the condensed state.

Dialkylhalonium ions can be prepared and even isolated as stable salts by reacting an excess of haloalkane with strong Lewis acid halides such as SbF_5 in low nucleophilicity solvent systems (such as SO_2CIF , SO_2 , etc.).

$$2 RX \xrightarrow{SbF_5} R \xrightarrow{-X^+} R SbF_5 X^-$$

$$X = Cl, Br and I$$

In superacid solutions, dialkylhalonium ions show extremely enhanced alkylating reactivity. This is considered due to the further protolytic (or electrophilic) activation involving the nonbonded electron pair of the halogen atoms leading to gitonic dicationic superelectrophiles.⁵

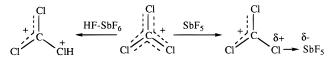
Similarly in the HF–SbF₅ superacid-catalyzed carbonylation reaction of alkanes, when Br^- ion was added into the reaction mixture, the reaction rate increased greatly as reported by Sommer et al.⁶ They considered it as a consequence of in situ

formation of Br⁺. Olah suggested,⁵ however, that the activation more probably is due to protolytic activation of H_2Br^+ via the gitonic trihydrobromonium dication H_3Br^{2+} .

$$H - Br \stackrel{H^+}{\longleftarrow} H \stackrel{Br^+}{\longrightarrow} H \stackrel{H^+}{\longleftarrow} \left[H \stackrel{Br^{2+}_{\dots, m}}{\longrightarrow} H \right]$$

Recently Boldyrev and Simons calculated⁷ the structures and energies of H_3X^{2+} and H_4X^{3+} (X = F, Cl, Br, and I) ions by ab initio methods. All doubly charged ions are found as stable minima on their potential energy surfaces. These dications also have considerable kinetic barrier for dissociations. Except for H_4F^{3+} , all triply charged ions also possess local minimum on their potential energy surfaces. But the trications are predicted to have very small deprotonation barriers. The trication H_4F^{3+} does not possess a local minimum on its potential energy surface.⁷

Halomethyl cations in superacid solutions also show greatly enhanced reactivities.^{8–12} If the nonbonded electron pairs of halogen atoms of these ions were affected by further protolytic (or electrophilic) interaction, the electron deficiency of the corresponding carbocationic centers would become more pronounced resulting in enhanced superelectrophilic reactivity. We recently reported¹³ theoretical investigation of the effects of protolytic activation on the properties of halomethyl cations.



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In continuation of our work we now report density functional theory (DFT)¹⁴ studies to investigate the electronic structure and properties of a series of methylhalonium ions and their protonated or methylated gitonic dications. Hydrogen/deuterium exchange experiment of dimethylbromonium ion, $(CH_3)_2Br^+$, in DF/SbF₅ superacid solution was also carried out. Besides activation of dimethylbromonium ion by bomine lone pair protonation, C–H protonation of the ion is also possible. C–H protonation of dimethylbromonium ion would lead to dication $CH_3Br^+CH_4^+$ 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-94¹⁵ 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 0.96¹⁶) level, if not stated otherwise. For X = I, the geometry and frequency calculations were performed at the B3LYP/LANL2DZ (D95¹⁷ on C and H, Los Alamos ECP plus DZ¹⁸ on Br or I) level. Calculated energetics will be given at the B3LYP/LANL2DZ + ZPE (at B3LYP/ LANL2DZ scaled by a factor of 0.96¹⁶) level, if not stated otherwise. The total energies of the calculated structures are shown in (Tables 1 and 2). Atomic charges and Löwdin¹⁹ bond order were obtained using the natural bond orbital analysis (NBO)²⁰ method (Figures 1 and 2).

 H_3X^{2+} (X = F, Cl, Br, I): DFT calculated structures of H_3X^{2+} as well as H_2X^+ agree well with the recently reported ab initio MP2(FU)/6-31G** structures of Boldyrev and Simons.7 C_{3v} symmetrical dications H₃Cl²⁺ **2b**, H₃Br²⁺ **2c**, and H₃I²⁺ **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_2X^+ and H^+ is exothermic by 66.9, 44.4, and 35.0 kcal/mol. On the other hand H_3F^{2+} 2a has a planar D_{3h} structure and has only 8.6 kcal/mol dissociation barrier. Trication 2a is also thermodynamically highly unstable toward dissociation into H₂F⁺ 1a and H⁺ by 106.4 kcal/mol. Lowdin 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

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Table 1. Energies (-au), ZPE^{*a*}, Relative Energies,^{*b*} and Proton Affinity

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

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

Table 2. Energies (-au), ZPE^{*a*}, Relative Energies,^{*b*} and Proton Affinity

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

^{*a*} Zero point vibrational energies (ZPE) in kcal/mol at B3LYP/ LANL2DZ level scaled by a factor of 0.96. ^{*b*} Relative energies based on B3LYP/LANL2DZ //B3LYP/LANL2DZ + ZPE.

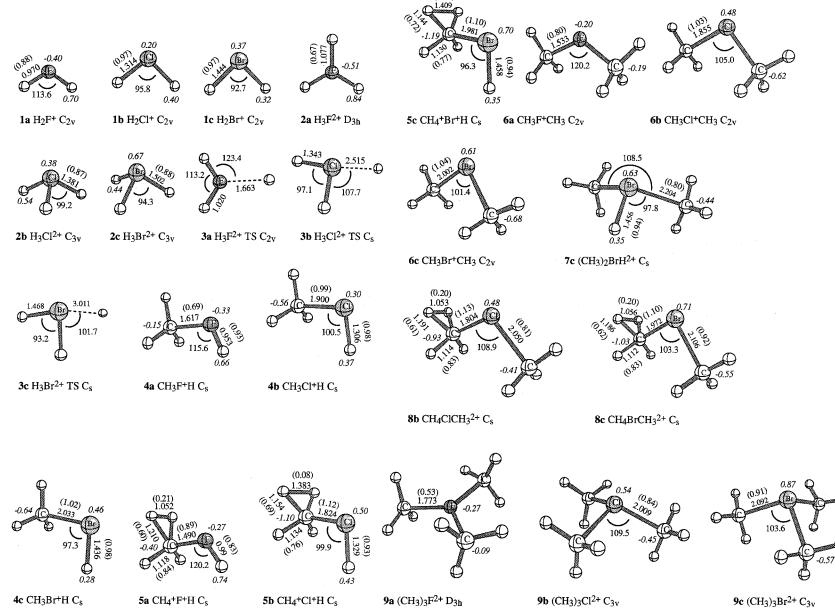
halogen atoms.² The electronegativities and size of the halogens atoms are also in line with the calculated proton affinities of the H_2X^+ ions (X = F -104.9, Cl -65.4, Br -42.9, I -33.5).

As mentioned, the greatly increased reactivity⁶ of the HF– SbF₅ superacid-catalyzed carbonylation of alkanes upon adding Br⁻ ion could be due to protolytic activation of H₂Br⁺ to gitonic H₃Br^{2+,5} Thermodynamically the H₃Br²⁺ dication is expected to be more stable in the solution than in the gas phase. Olah et al. reported⁵ experimental and theoretical studies of the H₄O²⁺ dication. In fact hydrogen–deuterium exchange experiments of isotopomeric H₃O⁺ 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 H₄O²⁺ dications. In comparison, the calculated proton affinity (PA) of H₂Br⁺ (-42.9 kcal/mol) is even more than PA of H₃O⁺ (-60.4 kcal/mol). On the other hand the calculated dissociation barrier of H₄O²⁺ (38.2 kcal/mol).

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

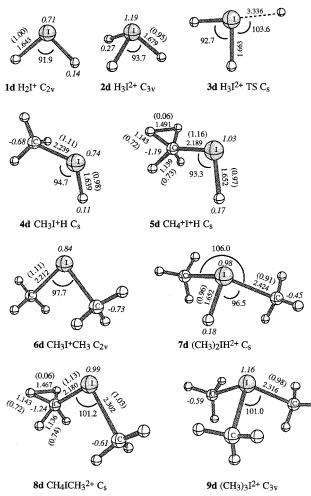


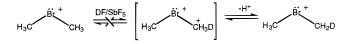
Figure 2. B3LYP/LANL2DZ calculated selected parameters, NBO charges (in italics), and Lowdin bond orders (in parentheses).

 CH_4XH^{2+} (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 CH₃XH₂²⁺ 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).

 $(CH_3)_2XH^{2+}$ and $CH_3X^+H(CH_4^+)$ (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- 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 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, (CH₃)₂Br⁺, was prepared by reacting excess methyl bromide with SbF₅ in SO₂ at -78 °C and characterized by ¹H and ¹³C NMR spectroscopy. $(CH_3)_2Br^+SbF_6^-$ salt was isolated from the solution by evaporating SO₂. Dimethylbromonium ion was treated with excess of 4:1 DF/SbF₅ superacid at -78 °C and was allowed to slowly warm to -20 °C. The 4:1 DF/SbF5 is one of the strongest superacid systems known.³ The resulting solution was periodically monitored by ¹H and ²H NMR spectroscopy to observe any hydrogen/deuterium exchange at the CH₃ groups of (CH₃)₂Br⁺. 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 (CH₃)₂Br⁺ ion was detected by ¹H and ²H NMR spectroscopy over a period of about 1 day (within the detection limit of NMR; $\leq 0.5\%$). To account for the absence of isotopic exchange, protonation (deuteration) of the (CH₃)₂Br⁺ ion at the methyl group can be excluded.



The enhanced reactivity of dimethylbromonium ion under superacid conditions,⁵ therefore, must be due to the formation of the superelectrophilic, gitonic Br-protonated dimethylbromonium dication $(CH_3)_2BrH^{2+}$ as the de facto reactive intermediate and not the C–H protonated $CH_3Br^+CH_4^+$. 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**.

$$H_{3}C \xrightarrow{BC} H_{3} \xrightarrow{DF/SbF_{5}} \left[H_{3}C \xrightarrow{BC} H_{3}C \xrightarrow{-D^{+}} H_{3}C \xrightarrow{BC} H_{3}C \xrightarrow{-D^{+}} H_{3}C \xrightarrow{BC} H_{3}C \xrightarrow{-D^{+}} H_{3}C \xrightarrow$$

Dimethylchloronium ion, $(CH_3)_2Cl^+$, was also treated with excess of 4:1 DF/SbF₅ 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 CH₃ groups of $(CH_3)_2Cl^+$. Similar to $(CH_3)_2Br^+$ ion, even at -10 °C no exchange products or decomposition of the $(CH_3)_2Cl^+$ 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 CH₃ groups of the long-lived trimethyloxonium ion, (CH₃)₃O⁺, when treated with excess DF/SbF₅ superacid.²¹ The lack of hydrogen/deuterium exchange in (CH₃)₃O⁺ is also consistent with theoretical calculations which showed that the O-protonated trimethyloxonium dication (CH₃)₃OH²⁺ is more stable than the C–H protonated (CH₃)₂O⁺CH₄⁺ by 31.2 kcal/ mol.²¹ Acetyl cation also showed similar behavior with Oprotonation preferred over C–H protonation in DF/SbF₅ 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*-butyl²² and 2-propyl cations,²³ can undergo C–H protonation to form highly electron deficient *protio*-alkyl dications.

 $(CH_3)_3 X^{2+}$ (X = F, Cl, Br, I): We also calculated the structures of methylated dimethylhalonium dications. The $C_{3\nu}$ symmetrical $(CH_3)_3 Cl^{2+}$ 9b, $(CH_3)_3 Br^{2+}$ 9c, and $(CH_3)_3 I^{2+}$ 9d were found to be the stable minima. The fluoro analogue $(CH_3)_3 F^{2+}$ 9a is also a minimum but has a planar D_{3h} 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 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.⁵ We previously reported^{24,25} that superelectrophilic activation offers an adequate explanation of the observed experimental data for a variety of superacid-

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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.⁵

Conclusions

Structures and energies of a series of diprotonated hydrogen halides (H₃X²⁺) and gitonic protio methyl- and dimethylhalonium dications (CH₃XH₂²⁺ and (CH₃)₂XH²⁺) 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, (CH₃)₂Br⁺ (as well as on the dimethylchloronium ion, (CH₃)₂Cl⁺ ion), by reacting (CH₃)₂-Br⁺ SbF₆⁻ with excess 4:1 DF/SbF₅ superacid at -20 °C as well as room temperature. No exchange was observed at the CH₃ groups of (CH₃)₂Br⁺ or (CH₃)₂Cl⁺ which would involve the intermediacy of the corresponding Br,C-protio (deuterio) dimethylbromonium dications. The lack of hydrogen/deuterium exchange was dicussed by using calculated data.

Experimental Section

Methyl bromide (Aldrich), methyl chloride, anhydrous HF (Setic Lab), D_2O (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_2O .²⁶ Benzoyl fluoride was prepared from benzoyl chloride and anhydrous HF as previously reported.²⁷

¹H and ²H 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_6 capillary as the external standard.

H/D Exchange Experiments with DF/SbF₅. (CH₃)₂Br⁺ SbF₆⁻ or (CH₃)₂Cl⁺ SbF₆⁻ (ca. 150 mg) was placed in a Kel-F tube and cooled to $-78 \,^{\circ}$ C in a dry ice/acetone bath. Approximately 2 mL of DF/SbF₅ (4:1 molar solution) was added at $-78 \,^{\circ}$ C. The ensuing mixture was vigorously stirred and (Vortex stirrer) was kept at $-20 \,^{\circ}$ C and periodically monitored by ¹H and ²H NMR spectroscopy.

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