Vicinal dihalonium ions: diprotonated and dimethylated chlorine [$H_2Cl_2^{2+}$, $(CH_3)_2Cl_2^{2+}$] and bromine [$H_2Br_2^{2+}$, $(CH_3)_2Br_2^{2+}$] dications

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High level ab initio calculations at the MP2/cc-pVTZ, CCSD(T)/cc-pVTZ, and CASSCF(6,6)/cc-pVTZ levels were performed to investigate geometries and energies of superelectrophilic diprotonated, and dimethylated molecular chlorine (Cl₂) and bromine (Br₂) dications. Diprotonated chlorine and diprotonated bromine dications 3a and 6a, respectively, were found to be lowest energy minima. The isomeric dications, 3b and 6b, are also minima on the potential energy surfaces but they are significantly less stable than the structures 3a and 6a by 33.6 and 30.9 kcal/mol, respectively. On the basis of computed G2 energies, proton affinities and related thermodynamic parameters were also calculated. Dications 3a and 6a have substantial kinetic barriers for deprotonation. Their homolytic dissociation are however facile. Dimethylated molecular chlorine and bromine dications 3g and 6g, respectively, were also found to be global energy minima. These vicinal dihalonium or the corresponding protosolvated species are expected to form either in the superacidic media or in the gas phase.

ab initio | halonium | superacid | gas phase

Halonium ions are an important class of onium ions (1). Their role as reaction intermediates (in halogenation, Friedel–Crafts alkylation reaction, etc.) and in preparative chemistry is well recognized. Dialkyl (aryl) halonium ions are closely related to the alkyloxonium ions (Meerwein salts) but offer better selectivity. Dialkylhalonium ions can be prepared as stable long-lived ions (1–3) in superacidic solution and can also be prepared and even isolated as stable salts by reacting an excess of haloalkane with strong Lewis acid halides such as SbF₅ in low nucleophilicity solvent systems (such as SO₂ClF, SO₂, etc.).

In superacid solutions, dialkylhalonium ions show extremely enhanced alkylating ability. This is considered to be due to further protolytic (or electrophilic) activation involving the nonbonded electron pair of the halogen atoms leading to gitonic dicationic superelectrophiles. (4)

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 Bukala et al. (5) They considered it as a consequence of in situ formation of Br⁺. Olah suggested (4), however, that the activation more probably is due to protolytic activation of H_2Br^+ via the gitonic (4) trihydrobromonium dication H_3Br^{2+} or corresponding protosolvation.
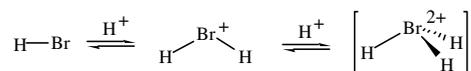
Boldyrev and Simons calculated (6) the structures and energies of H_3X^{2+} and H_4X^{3+} (X = F, Cl, Br, and I) ions by ab initio methods. All doubly charged ions were found as stable minima on their potential energy surfaces. These dications also have considerable kinetic barrier for dissociations. Except for H_4F^{3+}, all triply charged ions also possess local minimum on their potential energy surfaces. However, 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 (6). We have previously reported (7) theoretical and experimental investigation of the effects of protolytic activation on the properties of diprotonated hydrogen halides (H_3X^{2+}, X = Cl, and Br) and gitonic protio methyl- and dimethylhalonium dications [$CH_3XH_2^{2+}$ and $(CH_3)_2XH^{2+}$]. Hydrogen/deuterium exchange experiments were also carried out on the dimethylbromonium ion, $(CH_3)_2Br^+$ [as well as on the dimethylchloronium ion, $(CH_3)_2Cl^+$ ion] by reacting $(CH_3)_2Br^+$ SbF_6^- with excess 4:1 DF/SbF₅ superacid at −20 °C as well as room temperature (7). Halomethyl cations in superacid solutions also show greatly enhanced reactivities (8–12). We recently reported (13) theoretical investigation of the effects of protolytic or protosolvolytic activation on the properties of halomethyl cations.

Structures of monoprotonated molecular chlorine (HCl_2^+) and bromine (HBr_2^+) calculated at the HF/6-31G* level were previously reported by Li et al, which show that monoprotonated Cl₂ and Br₂ have singlet ground states (14). Cacace et al. later calculated the structures at the density functional theory B3LYP/6-311 + +(3df, 3dp) level (15). Experimental proton affinity (PA) of Cl₂ was found to be 131.4 kcal/mol at 298 K, which compares well with the 132.0 kcal/mol value computed at the CCSD(T) level of theory. (15) In continuation of our work, we now report high-level ab initio calculational studies to investigate the electronic structure and properties of diprotonated molecular chlorine (Cl₂) and bromine (Br₂), which have until now not been reported and are of substantial interest.

Calculations

The geometries were optimized at the MP2/cc-pVTZ, CCSD(T)/cc-pVTZ, and CASSCF(6,6)/cc-pVTZ levels. Vibrational frequencies at the respective levels were used to characterize stationary points as minima [number of imaginary frequency (NIMAG) = 0] or transition state [(NIMAG) = 1] and to evaluate zero point vibrational energies (ZPE), which were scaled by a factor of 0.95 in the case of MP2 calculations (16). For improved energy, relative energies were calculated based on Gaussian-2 (G2) theory. Calculated energies are given in Table 1. Atomic charges were obtained using the natural bond orbital analysis (NBO) (17) method. MP2/cc-pVTZ geometrical parameters and G2 calculated energies are discussed throughout, unless stated otherwise. The complete active space self-consistent field (CASSCF) wave function used in the calculation of the transition states **3d** and **6d** is characterized by an active space of six σ-electrons in six σ-orbitals (6e/6o). Active space for CASSCF

Table 1. Energies (-au), ZPE *, relative energies, and PA in kcal/mol

Ions	MP2/cc-pVTZ	ZPE	Rel. energy [†]	G2	Rel. energy [‡]	CCSD(T)	ZPE	Rel. energy[§]	PA
	chloro-								
1	919.37678	0.8	129.6	919.44221	130.9	919.42662	0.8	132	132.4
2	919.59115	5.7	0	919.65084	0	919.64513	5.9	0	−18.5
3a	919.56965	10.4	18.2	919.62372	17	919.62694	10.8	16.3	
3b	919.51487	10.4	52.6	919.57026	50.6	919.5773	10.8	50.2	
3c TS	919.47272	6.1	74.7	919.53304	73.9	919.52653	6.3	74.9	
3d TS	919.50765	8.1	54.8			919.59802 [¶]	8.7 [‖]	32.4	
3e TS	919.4881	8.2	67.2	919.54725	65	919.54616	8.7	64.9	
ClH⁺ · (x2)	919.68876	7.4	−59.5	919.74582	−59.6	919.75066	7.6	−64.5	
	bromo-								
4	5145.3612	0.5	144.5	5145.1413	145.8	141.9			
5	5145.5914	4.9	4.5	5145.3651	5.4	6.9			
6a	5145.6057	9.4	0	5145.3737	0				
6b	5145.554	9.6	32.6	5145.3244	30.9				
6c TS	5145.4876	5.3	70						
6d TS	5145.5447	7.5	36.4						
6e TS	5145.5306	7.8	45.9	5145.3033	44.1				
BrH⁺ · (x2)	5145.7121	7	−69.1	5145.4829	−68.5				

*ZPE in kcal/mol at MP2/cc-pVTZ level scaled by a factor of 0.95.
[†]Relative energies based on MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE.
[‡]Relative energies based on G2 energies.
[§]Relative energies based on CCSD(T)/cc-pVTZ energies + ZPE.
[¶]CCSD(T)/cc-pVTZ //CASSCF(6,6)/cc-pVTZ.
[‖]At CASSCF(6,6)/cc-pVTZ level.

calculations were the molecular orbitals σ/σ^* related to the bonds between X–X and X–H. Calculations were carried out with Gaussian 03 (18) programs.

Results and Discussion

Studies on $H_2Cl_2^{2+}$. MP2/cc-pVTZ calculated structures of Cl_2 **1** and HCl_2^+ **2** agree well with the reported B3LYP/6-311 + +(3df, 3dp) structures of Cacace et al. (15). MP2/cc-pVTZ calculated Cl–Cl bond distances in **1** and **2** are 1.997 and 1.999 Å, indicating little bond elongation (only 0.002 Å, 0.1%) upon protonation of Cl_2 (Fig. 1). Geometry optimization of these systems at CCSD(T) level shows that the MP2 calculation reflects the geometry well in these systems. Second protonation of HCl_2^+ **2** can occur on the terminal Cl atom to give dication **3a** or on the center Cl atom to give dication **3b**. Both structures were found to be minima on the potential energy surface (PES). However, energy comparison [computed with the G2 theory or CCSD(T)] shows that the structure **3b** is substantially less stable than the structure **3a** by 33.6 kcal/mol (G2) and 33.9 [CCSD(T)]. Structure **3a** resembles hydrogen peroxide with a dihedral angle (HClClH) of 97.5°. The Cl–Cl bond distance of 2.047 Å in **3a** is longer by 0.048 Å than that of monocation **2**, indicating also little Cl–Cl bond elongation (2.4%) in dication **3a** compared to monocation **2**. On the other hand, the structure **3b** has a pyramidalized chloronium atom with a Cl–Cl bond distance of 2.031 Å (Fig. 1).

Two dissociation paths, deprotonation through transition state **3c** and homolytic dissociation into two HCl^+ radical cations through transition state **3d** were calculated for the dication **3a**. The transition state **3d** for homolytic decomposition was located at CAS(6,6) level, because the inadequacy of a single configurational method for bond homolysis is well known. Deprotonation of **3a** is exothermic by 17.0 kcal/mol although it has a high kinetic barrier of 56.9 kcal/mol [58.6 kcal/mol at CCSD(T) level] through transition state **3c** (Table 1). On the other hand, homolytic dissociation of **3a** is also exothermic [76.6 kcal/mol (G2) and 80.8 kcal/mol (CCSD(T)] and also has a kinetic barrier of 16.3 kcal/mol [at the CCSD(T)/cc-pVTZ//CAS(6,6)/cc-pVTZ + ZPE level] through transition state **3d**. For the very floppy degrees of freedom such as the torsional motion around the Cl–Cl bond axis of **3a**, the use of a harmonic vibrational frequency to characterize the motion is probably questionable, especially in the determination of the relative energy. This, how-

ever, probably will not make great improvement because the barrier of Cl–Cl bond dissociation (16.3 kcal/mol) is quite substantial. These data indicate that, both thermodynamically and kinetically, the homolytic process is the preferable pathway for dissociation of dication **3a**. However, these dissociation energy values seem of significant magnitude, preventing the dissociation of the once formed dicationic species to the corresponding monocationic species (preferably at low temperatures). Pictorial representation of the PES involving the formation of dications **3a** from **2** is depicted in Fig. 2. Calculated vibrational frequencies of **1**, **2**, **3a**, and **3b** at MP2 level are given in Table 2.

We have also calculated the energy barrier involved in the isomerization of dication **3a** to **3b** through transition structure **3e** to be around 48 kcal/mol (Fig. 1 and Table 1). Although kinetically and thermodynamically less favored, once formed, dication **3a** is unlikely to undergo further rearrangement to give **3b**.

NBO charge calculations show that in protonated Cl_2 (**2**), the central chlorine atom carries a positive charge of +0.41 (Fig. 3) and the terminal chlorine atom with +0.24. This indicates that the positive charge of the central chlorine atom is diminished by the effect of the adjacent chlorine atom. Similar delocalization of the positive charge was also observed in the dication **3a**. In the dication **3a**, the two chlorine atoms carry a total of +1.16 charge and two hydrogen atoms +0.84. In the dication **3b**, the two chlorine atoms carry a total of +1.06 charge and two hydrogen atoms +0.94.

From the computed G2 energies, the proton affinity of **2** is estimated to be −18.5 kcal/mol [to give vicinal distonic (4) dication **3a**]. This value can be compared to that of the proton affinity of the oxonium ion H_3O^+ [−60.4 kcal/mol, to give gitonic (4) dication H_4O^{2+}] (19). It should be emphasized that the gas-phase calculations may not necessarily reflect the behavior in condensed phases. In the latter case, solvation effects may further stabilize the dicationic species allowing them to be observable under long-lived stable ion conditions in the superacid media (4). It should also be recognized that, in the condensed phase, electrophilic (protolytic) solvation (20) might have great influence. Superacid-activation reactions may proceed through superelectrophilic solvation without necessarily forming limiting dicationic intermediates (i.e, H-Cl⁺-Cl-----H⁺ or H-Cl⁺-Cl$^{\delta+}$-----LA$^{\delta-}$). Lewis acidic (LA) electrophiles are uncharged, and with these superelectrophilic solvation avoids charge–charge repulsion effects

Fig. 1. Calculated structures of **1**–**6**. Just numbers refers to MP2/cc-pVTZ calculations; between brackets are the values for CCSD(T); and in italics and between parentheses are the results for CASSCF(6,6).

(20). It is important to mention that, under suitable conditions, the parent oxonium dication (H_4O^{2+}) is indicated to be a stable species. Indeed, the hydrogen–deuterium exchange of H_3O^+ in superacidic media strongly supports the intermediacy of such dicationic species (4, 21). Calculated PA of HCl_2^+ **2** (−18.5 kcal/mol) is in fact much higher than PA of H_3O^+ (−60.4 kcal/mol). On the other hand, the calculated dissociation barrier of $H_2Cl_2^{2+}$ **2** (36.6 kcal/mol) is very close to the dissocia-

Fig. 2. Pictorial representation of the potential energy surface of dications **3a**.

tion barrier of H_4O^{2+} (38.2 kcal/mol) (19) implying that the distonic (4) dication **3a** can be an observable species in the superacidic media or in the gas-phase.

Studies on $(CH_3)_2Cl_2^{2+}$. For comparison, we also calculated the methylated analogues, $CH_3Cl_2^+$ and $(CH_3)_2Cl_2^{2+}$ at the MP2/cc-pVTZ level. Similar to protonated **2** and **3a**, methylated structures **3f** and **3g** were found to be minima on the potential energy surface of $CH_3Cl_2^+$ and $(CH_3)_2Cl_2^{2+}$, respectively. Calculated structure of **3f** and **3g** are depicted in Fig. 1. Attempts to find a minimum for the isomeric structure $(CH_3)_2Cl-Cl^{2+}$ (similar

Table 2. MP2/cc-pVTZ calculated frequencies* and IR intensities

No.	Frequencies in cm^{-1}(IR intensities in km/mole)
1	578 (0)
2	547 (0), 875 (16), 2766 (267)
3a	333 (95), 498 (0), 886 (84), 912 (1), 2493 (648), 2520 (345)
3b	426 (0), 742 (82), 751 (0), 1117 (43), 2286 (661), 2332 (597)
4	343 (0)
5	327 (0), 738 (6), 2565 (163)
6a	294 (32), 303 (27), 754 (46), 771 (1), 2384 (423), 2399 (250)
6b	258 (0), 646 (43), 653 (0), 1111 (26), 2236 (449), 2257 (435)

*Not scaled.

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+0.41   +0.24
Cl———Cl

H +0.35

2

+0.58   +0.58
Cl———Cl
        |||H
H +0.42   +0.42

3a

+0.47   +0.57   +0.49
H|||||Cl———Cl

H +0.47

3b

+0.49   +0.28
Br———Br

H +0.23

4

+0.67   +0.67
Br———Br
        |||H
H +0.33   +0.33

5a
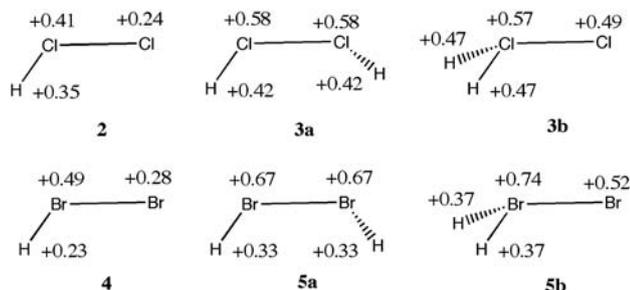
+0.74   +0.52
+0.37   Br———Br
H|||||
H +0.37

5b

Fig. 3. MP2/cc-pVTZ//MP2/cc-pVTZ calculated NBO charges of **2–5**.

to structure **3b**) have failed because of dissociation into more stable $CH_3Cl_2^+$ and CH_3^+ upon optimization.

Studies on $H_2Br_2^{2+}$. MP2/cc-pVTZ calculated Br–Br bond distances in Br_2 **4** and HBr_2^+ **5** are 2.277 and 2.281 Å (Fig. 1). This also shows, similar to chloronium system, little bond elongation (only 0.004 Å, 0.2%) upon protonation of Br_2. Second protonation of HBr_2^+ **5** can occur on the terminal bromine atom to give dication **6a** or on central bromine atom to give dication **6b**. Both structures were found to be minima on the PES. Structure **6b** is significantly less stable than the structure **6a** by 30.9 kcal/mol. Structure **6a** also resembles hydrogen peroxide with the HBrBrH dihedral angle of 94.3. The Br–Br bond distance of 2.332 Å in **6a** is longer by 0.051 Å than that in the monocation **5**. The Br–Br bond elongation in dication **6a** compared to monocation **5** was found to be only 2.2%. The structure **6b** has a pyramidalized bromine atom with a comparable Br–Br bond distance of 2.230 Å (Fig. 1). Calculated vibrational frequencies of **4**, **5**, **6a**, and **6b** are given in Table 2.

Unlike the chlorine system, deprotonation of **6a** is slightly endothermic by 5.4 kcal/mol and the process has a high kinetic barrier of 70.0 kcal/mol (at the MP2/cc-pVTZ//MP2/cc-pVTZ+ZPE level) through transition state **6c** (Table 1). Homolytic dissociation of **6a** into two HBr^+ radical cations, on the other hand, is exothermic by 68.5 kcal/mol and it also has a substantial kinetic barrier of 36.4 kcal/mol (at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level) through transition state **6d**. However, CAS(6,6) barrier predicts this barrier to be only 5.7 kcal/mol. Thus the homolytic dissociation process is also the favorable pathway for the cleavage of dication **6a**. Isomerization of the dication, **6a** to **6b** through transition structure **6e** has a 44.1 kcal/mol barrier (Fig. 1 and Table 1). Calculated PA of HBr_2^+ **5** (6.9 kcal/mol) is higher than PA of HCl_2^+ **2** (−18.5 kcal/mol). This difference in proton affinity is consistent with the order of the electronegativities (Cl > Br) and also the order of the size (Br > Cl) of chlorine vs. bromine. As mentioned, the hydrogen–deuterium exchange of H_3O^+ in superacidic media strongly supports the intermediacy of H_4O^{2+} dication (4, 21). Calculated PA of HBr_2^+ **5** (6.9 kcal/mol) is in fact much higher

than PA of H_3O^+ (−60.4 kcal/mol). On the other hand, the calculated dissociation barrier of $H_2Br_2^{2+}$ **6a** (36.4 kcal/mol) is close to the dissociation barrier of H_4O^{2+} (38.2 kcal/mol) (19), implying that the distonic (4) dication **6a** should be an observable species in the superacidic media or in the gas-phase.

NBO charge calculations show that, in protonated Br_2 (**5**), the central bromine atom carries a positive charge of +0.49 and the terminal chlorine carries a positive charge of +0.28 (Fig. 3). In dication **6a**, two bromine atoms carry a total of +1.34 charge and two hydrogens carry a total of only +0.66. This also shows dissipation of the positive charge in the vicinal halogen atom. In the dication **6b**, the two chlorine atoms carry a total of +1.26 charge and two hydrogen atoms +0.74. However, relative to chlorine, bromine carries more charge than hydrogen in both mono- and dications. This is again consistent with the order of the electronegativities (Cl > Br) and also the size (Br > Cl) of chlorine and bromine.

Studies on $(CH_3)_2Br_2^{2+}$. For comparison, we have also calculated the methylated analogues, CH3Br2+ and $(CH_3)_2Br_2^{2+}$, at the MP2/cc-pVTZ level. Structures **6f** and **6g** were found to be minima on the potential energy surface of $CH_3Br_2^+$ and $(CH_3)_2Br_2^{2+}$, respectively, and are depicted in Fig. 1. Attempts to find a minimum for the isomeric structure $(CH_3)_2Br-Br^{2+}$ (similar to structure **6b**) have failed because of dissociation into more stable $CH_3Br_2^+$ and CH_3^+ systems upon optimization.

Conclusions

High level ab initio calculations show that the diprotonated molecular chlorine and bromine (**3a** and **6a**) as well as dimethylated analogues (**3g** and **6g**) do exist as stable minima. Diprotonated structures **3a** and **6a** have significantly high activation barriers for their deprotonation to give the corresponding monocations, **2** and **5**, respectively. They have also activation barriers for homolytic dissociations that cannot be overcome at low temperatures. The isomeric dications, **3b** and **6b**, are also energy minima on the PES but are significantly less stable than the structures **3a** and **6a** by 33.4 and 30.9 kcal/mol, respectively. The proton affinity of HCl_2^+ **2** (to give **3a**) and HBr_2^+ **5** (to give **6a**) are substantially higher than that of H_3O^+ (to give H_4O^{2+}), indicating that, under appropriate gas-phase or superacidic conditions, the dicationic species **3a** and **6a** should be observable species. Our study raises the possibility for experimental observation of vicinal dihalonium ions ($HXXH^{2+}$ and $CH_3XXCH_3^{2+}$) in low nucleophilicity superacid systems, as they are also related to previously studied diprotonated hydrazine and hydrogen peroxide ($H_3NNH_3^{2+}$ and $H_2OOH_2^{2+}$).

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