Trihalomethyl Cations: Relative Stability of CX_3^+ (X = F, Cl or Br)

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Calculations at the MP4/6-31G*//MP2/6-31G* level predict that the order of stability of trihalomethyl cations (CX_3^+) is Cl > Br >> F.

Olah *et al.* have recently attempted to isolate trihalomethyl cations such as CF_3^+ **1**, CCl_3^+ **2** and CBr_3^+ **3** under superacid conditions.[1] While they successfully isolated the chloro- and bromo-cations **2** and **3**, they were unsuccessful in isolating the fluoro-cation **1**. This is surprising since **1** was expected to be most stable because of superior overlap between the F 2p and C 2p atomic orbitals.[2,3] Further, CF_3^+ is a stable species in the gas phase,[4] which is readily formed during mass spectral analysis of fluorinated organic compounds.

In order to obtain an independent estimate of the stability of these trihalomethyl cations, particularly **1**, the relative hydride affinities of **1–3** have been calculated using *ab initio* molecular orbital theory.[5] All stationary points were optimized at the MP2/6-31G*[6] level except for the bromides where a valence double zeta pseudopotential basis set (LANL1DZ)[7] was used. Finally, single point MP4(SDTQ) energies were computed at the MP2 geometries. All three structures are true minimia having only positive force constants.†

The computed energies and relative hydride affinities (HA) for **1–3** are given in Tables 1 and 2, respectively. The HAs of CH_3^+ and $C_4H_9^+$ are also given for comparison. The trichloro-cation **2** is calculated to be 33.7 kcal mol^{-1} (1 cal = 4.184 J) more stable than the trifluoro-cation **1**. The tribromo-cation **3** is 1.6 kcal mol^{-1} less stable than **2**, but this number is less certain since pseudopotentials were used in calculating the energy of **3**. Cations **1** and **2** are directly comparable, however, and it is surprising that **1** is found to be so much less stable than **2**. As stated earlier, it is often argued that fluorine is the best

Table 1 Total energies in hartrees

Structure	MP2/6-31G*	MP4(SDTQ)[a]
1	−336.4425330	−336.4578605
2	−1416.5047309	−1416.5277515
3	−76.4256119[b]	−76.4526230[b]
CF_3H	−337.4189848	−337.4359549
CCl_3H	−1417.4294497	−1417.4522710
CBr_3H	−77.3541809	−77.3796408

[a] Computed at the MP2 geometry. [b] LANL1DZ basis set.

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† Force constants were calculated at the MP2 level for **1** and **2**, and at the HF level for **3**.

Table 2 Relative hydride affinities in kcal mol^{-1}

Structure	MP2/6-31G*	MP4(SDTQ)^a
1	55.4	56.3
2	23.0	22.6
3	25.4^b	24.2^b
CH_3+	75.0	75.4
C_4H_9+	0.0	0.0
CH_2F^+	49.5	
CH_2Cl^+	45.5	

^{a} Computed at the MP2 geometry. ^{b} LANL1DZ basis set.

Table 3 Calculated *ab initio* and AM1 charges

	MP4/6-31G*//MP2/6-31G*		AM1	
Structure	*C*	*X*	*C*	*X*
1	1.30	−0.10	0.71	0.10
2	−0.17	0.39	0.02	0.32
3	−0.29	0.43	−0.28	0.43

halogen at stabilizing adjacent carbocations owing to its superior π donating ability.[1–3] Theoretical calculations for $C_2H_4X^+$ indicate that fluorine is as capable as chlorine at stabilizing α-cations.[8] There is contrary experimental evidence that $C_2H_4Cl^+$ is favoured over $C_2H_4F^+$ by 4 kcal mol^{-1},[9,10] but this difference is insignificant compared to the 34 kcal mol^{-1} energy preference found for **2** over **1**.

Since the results change little upon going from MP2 to MP4, and since a rather large basis set is employed, it is difficult to believe that the very large energy preference found for **2** over **1** is simply an artefact of the calculation. In addition, this result is consistent with the superacid study[1] in which Olah *et al.* were able to generate **2**, but not **1**. Of course, we must be cautious when comparing the computed (gas phase) and superacid results because of the effect of solvent. In fact the solvation enthalpies for **1** and **2** should differ given the difference in their computed charges (Table 3). The positive charge in **1** is localized on the central carbon whereas in **2** it is distributed among the chlorines. This concentration of charge in **1** might lead to a more negative solvation energy compared to **2**. Nevertheless, given the 34 kcal mol^{-1} preference for **2** over **1** found in the gas phase, it is not surprising that **1** is apparently also less stable than **2** in superacid solution. What about the observation of CF_3^+ **1** in mass spectral studies? These calculations do find **1** to be a genuine minimum. Therefore, they are consistent with **1** being formed under the relatively extreme conditions typical of mass spectrometry. After all, **1** is found to be more stable than CH_3^+.

These results call into question the conventional wisdom that fluorine is better than chlorine at stabilizing an adjacent cation. Certainly, this is not the case for CX_3^+. It may be that, as additional fluorines are placed adjacent to the cationic centre, the electron-withdrawing power of fluorine simply overwhelms its π-donating ability. Calculations for CH_2X^+ (X = F or Cl) support this interpretation. The mono-fluoro-cation is computed to be only 4 kcal mol^{-1} less stable than the mono-chloro-cation at the MP2/6-31G* level (Table 2). Thus, comparison to **1** and **2** shows that substitution of two additional halogens for hydrogen leads to a 22.5 kcal mol^{-1} increase in stability for the less electronegative chlorides, and a 5.9 kcal mol^{-1} decrease in stability for the more electronegative fluorides. This divergence in behaviour upon increasing halogen substitution is responsible for the very large gap in stabilities found for **1** and **2**.

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