# Protonated β-Halogenoethyl Radicals

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*Ab initio* molecular orbital calculations suggest that protonated β-halogenoethyl radicals have an unsymmetrically bridged, nonclassical structure, in contrast to their neutral counterparts, which are predicted to be significantly more basic than the corresponding halogenoethanes.

The question of bridging in β-halogenoethyl radicals has received considerable experimental attention,[1—3] although theoretical work has consistently favoured classical open structures.[4—8] It has been pointed out that the symmetrical approach of a radical towards the centre of a double bond (to give a bridged radical) is 'exchange forbidden,' in contrast to the so-called colinear approach, which leads to a classical radical.[4] However, the bonding in symmetrically bridged radicals arises from a three-electron interaction between the radical singly occupied molecular orbital (SOMO) and the alkene π-orbital. This type of interaction has been shown[9—11] to be particularly favourable in radical ions, but far less so in neutral radicals. We therefore expected that protonation of β-halogenoethyl radicals should lead to a stabilisation of the bridged form, as has been found for β-amino- and hydroxyethyl radicals.[5,6]

Geometry optimisations with the 6–31G* basis set[12] followed by single point MP2/6–31G* energy calculations† confirm these predictions. The total and relative energies obtained are shown in Table 1. The β-fluoroethyl radical

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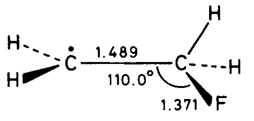
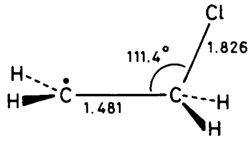
† The GAUSSIAN 82 (J. S. Binkley, R. A. Whiteside, K. Raghavachari, R. Seeger, D. J. De Frees, H. B. Schlegel, M. J. Frisch, J. A. Pople, and L. A. Khan, Carnegie-Mellon University, 1982) series of programs adapted for C.D.C. computers by Dr. A. Sawaryn and T. Kovar was used throughout. All calculations used the unrestricted Hartree–Fock formalism. Optimisations were carried out within the symmetry constraints given. MP2 calculations (C. Møller and M. S. Plesset, *Phys. Rev.*, 1974, **46**, 1423; J. S. Binkley and J. A. Pople, *Int. J. Quant. Chem., Symp.*, 1974, **9**, 229; J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quant. Chem.*, 1976, **10**, 1) did not include non-valence orbitals.

**Table 1.** Total (atomic units) and relative (kcal mol$^{-1}$, in parentheses) energies for the species (**1**)—(**10**).

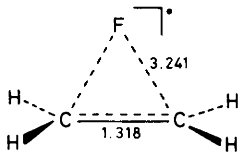
| | UHF/6-31G*//6-31G* | | MP2/6-31G*//6-31G* | |
|---|---|---|---|---|
| $C_2H_4 + F^{\cdot}$ | −177.39668 | (0.0) | −177.77158 | (0.0) |
| (**1**) | −177.44315 | (−29.2) | −177.84572 | (−46.5) |
| (**3**) | −177.39770 | (−0.6) | −177.77361 | (−1.3) |
| $C_2H_4 + Cl^{\cdot}$ | −537.47968 | (0.0) | −537.83678 | (0.0) |
| (**2**) | −537.49972 | (−12.6) | −537.86393 | (−17.0) |
| (**4**) | −537.48170 | (−1.3) | −537.84088 | (−2.6) |
| $C_2H_4^{\cdot+} + HF$ | −177.71462 | (0.0) | −178.09875 | (0.0) |
| (**5**) | −177.73298 | (−11.52) | −178.11948 | (−13.01) |
| (**7**) | −177.73284 | (−11.43) | −178.11940 | (−12.96) |
| (**9**) | −177.69576 | (11.8) | −178.08343 | (9.6) |
| $C_2H_4^{\cdot+} + HCl$ | −537.76833 | (0.0) | −538.10941 | (0.0) |
| (**6**) | −537.78023 | (−7.5) | −538.12033 | (−6.9) |
| (**8**) | −537.77893 | (−6.9) | −538.11782 | (−5.3) |
| (**10**) | −537.74602 | (14.0) | −538.10365 | (3.6) |



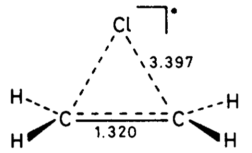
(**1**) $C_1$



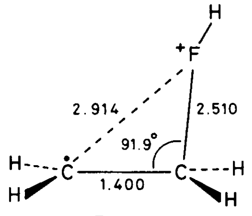
(**2**) $C_s$



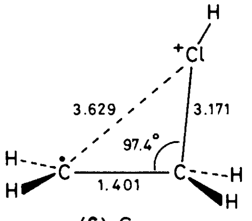
(**3**) $C_{2v}$



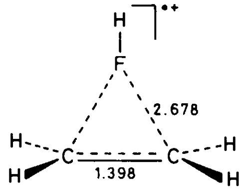
(**4**) $C_{2v}$



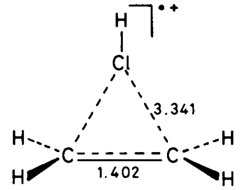
(**5**) $C_s$



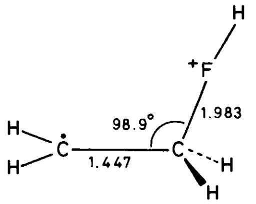
(**6**) $C_s$



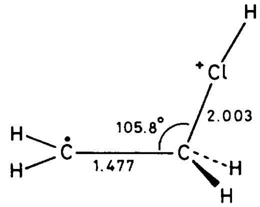
(**7**) $C_{2v}$



(**8**) $C_{2v}$



(**9**) $C_s$



(**10**) $C_s$

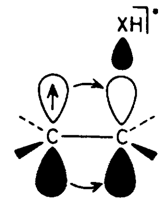
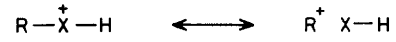
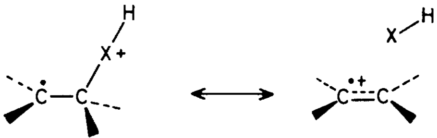


**Figure 1**



$R{-}\overset{+}{X}{-}H \longleftrightarrow \overset{+}{R}\ X{-}H$

(**11**)



(**12**)

prefers the $C_1$ structure (**1**) in which a carbon–hydrogen bond is eclipsed with the axis of the SOMO, rather than the carbon–fluorine bond. The $C_s$ structure (**2**) found for the β-chloroethyl radical is similar to those found previously.[4—8] The corresponding bridged structures (**3**) and (**4**) are found to be 44.9 and 14.4 kcal mol$^{-1}$‡ less stable than their open counterparts, respectively, but to be weakly bound relative to ethylene and a halogen atom, in contrast to the results of a recent MCSCF study.[7]

The protonated β-fluoro- and chloroethyl radicals (**5**) and (**6**) show distorted, unsymmetrically bridged structures with C–C–halogen angles around 90°. The $C_{2v}$ bridged structures (**7**) and (**8**) are calculated to be only 0.05 and 1.57 kcal mol$^{-1}$, respectively, less stable than the $C_s$ forms, and are clearly bound relative to the ethylene radical cation and the appropriate hydrogen halide. The orthogonal forms (**9**) and (**10**) are calculated to be 22.6 and 10.5 kcal mol$^{-1}$ less stable than (**5**) and (**6**), respectively, indicating a considerable degree of double bond character in the protonated radicals.

This double bond character arises from donation from a hypothetical localised radical SOMO into the $\sigma_{cx}^*$ orbital, Figure 1, which is enormously stabilized on protonation because of the positive charge and the weakening of the CX bond (the CF bond length in ethyl fluoride increases from

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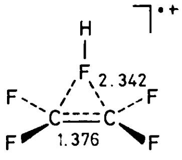
‡ 1 kcal = 4.184 kJ.



**(13)**, $C_2$

1.373 to 2.084 Å on protonation; the corresponding lengths for ethyl chloride are 1.799 and 2.154 Å). The $\sigma_{cx}^*$ orbital therefore becomes a good acceptor for the non-bonding electron and the CCX angle decreases. The result is a partial C–C π-bond and even more pronounced dissociation of the HX fragment than in the protonated alkyl halides. In valence bond terms, the 'no bond resonance' form (**12**) in the protonated radical is more important (because of the π-bond stabilisation) than the equivalent form (**11**) in the saturated molecules.

The stabilising effect of charge on the three-centre-three-electron bond in bridged radicals has one further effect, which may also have practical consequences. The calculated proton affinity of (**2**) (160.9 kcal mol$^{-1}$) is 7.4 kcal mol$^{-1}$ higher than that of ethyl chloride, and that of (**1**) (171.8 kcal mol$^{-1}$) 17.3 kcal mol$^{-1}$ higher than that of ethyl fluoride (MP2/6–31G*//6–31G* values throughout). These differences correspond to several p$K_a$ units when converted into the corresponding species in solution,[13] and suggest that the radical chemistry of alkyl halides in strong acids may show some unusual trends.

Finally we note that the tetrafluoroethylene radical cation forms a symmetrically bridged complex with the fluorine ligand of $CCl_3F$.[14] The protonated pentafluoroethyl radical (**13**) is also calculated (UHF/3–21G)[15] to have a symmetrically bridged structure.

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