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Original Investigations

Quantum Chemical Studies on Electrophilic Addition

IV. Reaction of the Nitrenium Ion with Ethylene and a Comparison of the Effectiveness of NH_2, OH, F, Cl and SH as Bridging Substituents

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The geometries of the 2-aminoethyl cation and the isomeric protonated aziridine have been optimized using *ab initio* molecular orbital calculations employing the split-valence shell 4-31G basis set. The protonated aziridine is computed to be the more stable ion by 46.5 kcal/mole (4-31G level) and 44.9 kcal/mole (double-zeta basis set). The profile to interconversion is found to have a barrier of less than 15 kcal/mole (relative to the 2-aminoethyl cation) and this profile is compared with those computed for the similar ions $XCH_2CH_2^+$ where X = OH, F, SH and Cl.

Key words: 2-aminoethyl cation – Aziridine, protonated ~ .

1. Introduction

The mechanism of electrophilic addition of a cation X^+, or incipient cationic species, XY, to both carbon-carbon double and triple bonds has been widely investigated both experimentally [1–7] and theoretically [8–22]. The usual reaction sequence is believed to consist of a slow step in which the neutral molecule, XY forms a carbonium ion and an anion, followed by a fast combination of the two ions (see Scheme 1). The structure of the intermediate carbonium ion, particularly the question as to whether it is a cyclic (I) or open (II) cation, has been the subject of considerable debate. Initially the electrophile XY is probably attracted towards the centre of the electron-rich π-bond forming the bridged structure I, but this may collapse with or without activation energy into the open cation II. Stable cations with the cyclic structure have been observed experimentally for X = SR [23–25] and also for X = Cl [26, 27] and OR [28] at low temperatures. Formation of the

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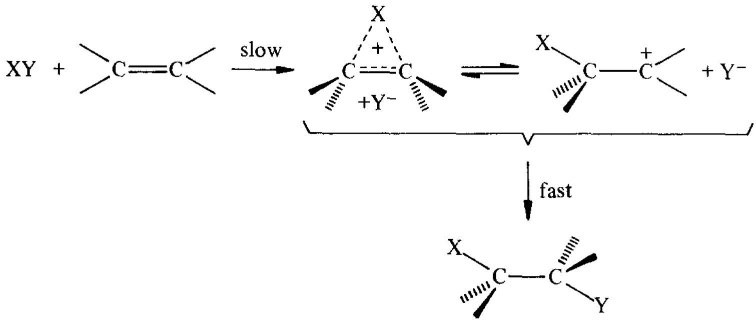
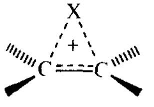
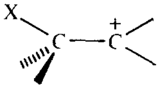


Scheme 1



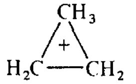
I



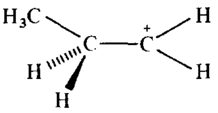
II

open cation, II, is promoted both by the presence of carbenium ion stabilizing alkyl or aryl groups in the alkene and also by electrophiles which are small (e.g. F^+, H^+) and are therefore ineffective in bonding with two carbon atoms simultaneously to form a three-membered ring.

Previous theoretical studies [9, 10, 14, 15] have shown that elements from the second row of the periodic table (S and Cl) are more effective than first-row elements from the same groups (O and F) at stabilizing the cyclic ion relative to the open cation. Furthermore, comparing groups within the *same* row the more polarizable group-six elements (O and S) are better atoms for bridging than the group-seven elements (F and Cl). These generalizations hold for additions of X^+ to both acetylene and ethylene, and with the latter substrate theoretical calculations [10, 14, 15] predict the cyclic chloronium, oxiranium and thiiranium ions to be more stable than the corresponding open cations. An extension of these general trends to the equilibrium between corner-protonated cyclopropane (III) and the 1-propyl cation (IV) would suggest that the bridged species, (III), should be considerably the more stable. However *ab initio* molecular orbital calculations at the SCF level have shown corner-protonated cyclopropane to have almost the same energy as the 1-propyl cation (the computed difference is 1.0 kcal/mole at the 6-31G* level with the cyclic ion the more stable [29, 30]).[1] Furthermore, the migration of the methyl group via the corner-protonated cyclopropane was shown to have no barrier. This profile to



III



IV

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[1] More sophisticated calculations including electron correlation show the non-classical corner-protonated cyclopropane to be more stable than the *n*-propyl cation by 9 kcal/mole [16].

interconversion is different from those computed for the heteroatom bridged ions and also does not follow the trend observed for elements in a particular row of the periodic table. This anomalous behaviour, coupled with the desire to examine the ability of nitrogen to stabilize bridged ions, has prompted us to complete our studies [9, 10, 14, 15] of the interconversion of bridged and open cations by examining the reaction of the nitrenium ion, $X = NH_2^+$, with ethylene.

The angle of approach of singlet methylene (isoelectronic with nitrenium ion) and the energy profile as a function of distance from the centre of the carbon-carbon bond of ethylene has been studied theoretically [31–33]. Addition of CH_2 preserving C_{2v} symmetry is forbidden according to the Woodward–Hoffmann rules [31], but MINDO/2 calculations show the barrier to be only 6 kcal/mole [32]. Both extended Hückel [31] and *ab initio* calculations with inclusion of valence shell electron correlation in the CEPA method [33] show that at large separations the ethylene and methylene moieties are in parallel planes (C_s symmetry) with the initial interaction being π-donation from the ethylene to the empty π-orbital of methylene. This phase is typical of electrophilic addition to ethylene. At closer distances, in the nucleophilic phase of the reaction, the lone pair of the methylene interacts with the π^* of the ethylene and the geometry reverts to C_{2v} symmetry and relaxes into cyclopropane. Both the extended Hückel and the much more sophisticated CEPA calculations showed there to be no barrier to this reaction. The presence of the positive charge in the interaction of the nitrenium ion with ethylene would be expected to lower the barrier to addition relative to that of the isoelectronic but neutral methylene and ethylene system. Since the most accurate calculations on this latter system show no barrier we concluded that there would be no barrier to the approach of NH_2^+ to ethylene and we did not perform any calculations on this aspect of the addition reaction.

2. Computational Details

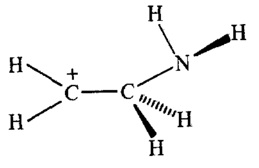
The geometry optimization of the 2-aminoethyl cation, protonated aziridine, and aziridine were carried out using the optimization procedure built into the GAUSSIAN 70 program [34]. The split-valence shell 4-31G basis set [35, 36] was employed for the optimizations. More accurate wavefunctions were computed for the optimum structures using Dunning's double-zeta contraction $((9^s5^p/4^s) \rightarrow [4^s2^p/2^s])$ [37] of Huzinaga's basis set [38]. The extended basis set wavefunctions were computed using a modified version [39] of the POLYATOM II program [40].

3. Results and Discussion

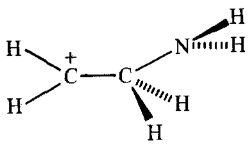
3.1. Geometry Optimization

Few experimental geometries are available for organic cations making it difficult to estimate reliable geometries. It was therefore necessary to carry out geometry optimizations on the cations.

A preliminary study of the profile to rotation about the C–N bond of the 2-aminoethyl cation (II, $X = NH_2$), maintaining a fixed pyramidal geometry for the



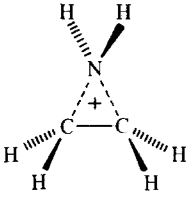
V



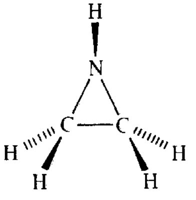
VI

amino group, established that both the maximum and the low minimum on the profile correspond to eclipsed structures V and VI respectively. The overall barrier to rotation using these non-optimum structures was found to be 16 kcal/mole. The most stable rotamer, VI, has a plane of symmetry with the two amino hydrogens removed as far as possible from the trigonal carbon atom. In terms of localized structures this places the nitrogen lone pair of electrons coplanar with the terminal methylene group. Both V and VI were taken to have the eclipsed conformation for C–N about the C–C bond, since electronegative substituents have been shown to occupy this conformation preferentially [9, 10, 15, 41–44], and consequently in structure VI the in-plane nitrogen lone pair cannot be delocalized into the formally vacant out-of-plane *p*-orbital of the methylene group. The high stability of this particular conformation then is most easily explained in terms of cancellation of internal dipole moments of the NH_2 group and the C–C bond, rather than by direct interaction of the lone pair with the electron deficient centre.

Full geometry optimizations were carried out on conformation VI of the 2-aminoethyl cation, on the aziridinium cation VII and on aziridine VIII, using the 4-31G basis set. In order to economize on computer time in the optimization procedure, the following assumptions were made. 1) The C—H bond lengths of the terminal methylene group of VI were assumed to be the same, although the bond angles, $\measuredangle$CCH were optimized separately. 2) The four hydrogen atoms attached to the carbon atoms of aziridine (VIII) were assumed to have identical geometrical parameters, thereby neglecting the small angle of twist observed experimentally [45] (and also reproduced by molecular orbital calculations at the STO-3G level) [46]. 3) Protonated aziridine was assumed to belong to the C_{2v} point group. The optimizations, varying each geometric parameter in turn, were terminated when subsequent changes failed to improve the energy by 1×10^{-5} hartree.



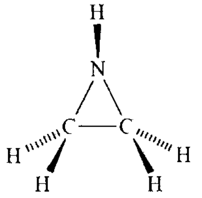
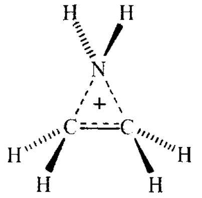
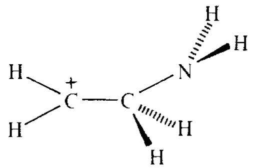
VII



VIII

The 4-31G energies generated for the 2-aminoethyl cation and aziridine (Table 1) were 0.00218 and 0.00302 hartrees respectively better than previous calculations at this level employing assumed [44] and STO-3G optimized geometries [46]. The

Table 1. Total energies (hartree) as computed with the geometry optimized with the 4-31G basis set

Species	STO-3G	4-31G	$(9^s5^p/4^s) \rightarrow [4^s2^p/2^s]$
	—	−132.82278	−132.98407
	−131.82028	−133.20751	−133.36494
	−131.71203	−133.13344	−133.29347

geometry optimized for aziridine is in good agreement with both the experimental [45] and STO-3G optimized [46] geometries.

Comparison of the optimized geometries of aziridine and its conjugate acid (Fig. 1) reveals that protonation on nitrogen produces an elongation of the C—N distance (by 0.05 Å) and a much smaller decrease of the C—C bond length (0.009 Å). Similar, but more pronounced changes were found to occur in the protonation of oxirane [15].

Comparison of the 4-31G optimized geometries of the β-substituted ethyl cations for X = F, OH, NH_2 and Cl revealed that, contrary to previous speculations [49], the carbon-carbon distance is essentially constant (~1.45 Å) for all substituents and is intermediate between the lengths of a single (1.54 Å) and a double (1.34 Å) bond. The C—X bonds in the β-X-substituted-ethyl cations also do not differ significantly or in a systematic way from those of the corresponding X-substituted ethanes.

3.2. *Rotational Barrier about the C-C Bond in the 2-Aminoethyl Cation*

The rotational barrier in the ethyl cation was computed to be small (zero at the STO-3G level) [47, 48]. Replacement of a β-hydrogen by an electron-withdrawing

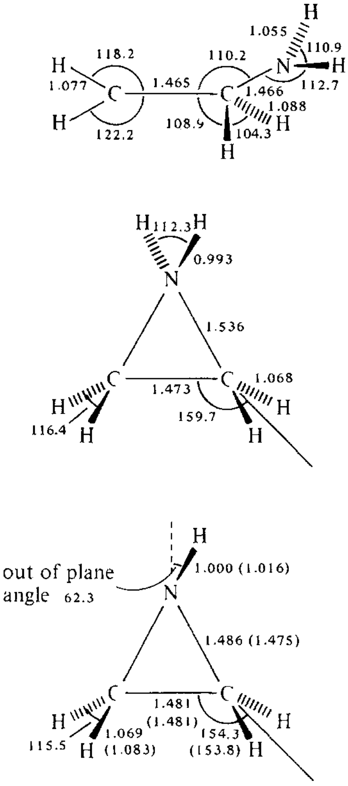
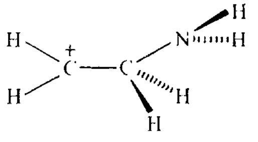
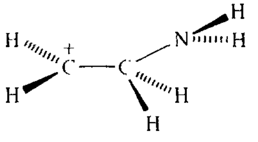


Fig. 1. Computed optimum geometries for 2-aminoethyl cation, aziridinium cation and aziridine. Bond lengths are in angstroms and bond lengths are in degrees. Parameters in brackets for aziridine are experimental values (Ref. [39])

substituent results in a much larger barrier with the eclipsed structure VI being more stable than the bisected structure IX. The barrier to this rotational profile for the 2-aminoethyl cation (6.2 and 12.5 kcal/mole respectively for the 4-31G and double-zeta calculations) is smaller than those computed for the 2-fluoro- and 2-hydroxyethyl cations, but is larger than that computed for the 2-chloroethyl cation (Table 2).


VI


IX

The origin of this barrier lies in the hyperconjugative interaction of the formally empty p-orbital on the carbon atom of the methylene group with the CH_2X group. In the eclipsed conformation the empty p-orbital interacts with the appropriate combination of orbitals on the two hydrogen atoms, while in the bisected form it

Table 2. Barriers for rotation about C—C$^+$ (kcal/mole) for β-substituted ethyl cations

Substituent	4–31G[a]	Double-zeta
NH_2	7.7, 0.4[b]	12.5
OH	11.4	15.0[c]
F	14.0	17.6[d]
Cl	—	6.5[e]

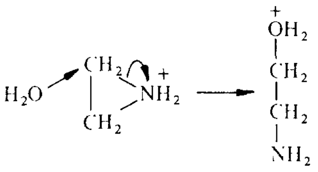
[a] Ref. [44].
[b] Barrier depends on conformation of amino group which was taken to be planar.
[c] Ref. [15]. [d] Ref. [9]. [e] Ref. [10].

interacts mainly with the C—X bond. In the latter conformation, when the substituent X is more electronegative than hydrogen as in the case of the amino group, the interaction between the "empty" p-orbital and the CH_2X group is then less stabilizing than the interaction in the eclipsed conformation. If this hypothesis is correct then the barrier to rotation about the C—C bond should decrease with decreasing electronegativity of the substituent X and such behaviour has, in fact, been observed (see Table 2). Furthermore introduction of groups less electronegative than hydrogen (e.g. Li, BeH and BH_2) into the β-position result in the bisected conformation being the more stable [44].

3.3. *Profile for Interconversion of Open and Cyclic Ions*

The profile to interconversion of the 2-aminoethyl and protonated aziridine cations was constructed by assuming that all the atoms move in a synchronous fashion. Thus, for example, a point 25% along the reaction path has bond lengths and angles which are 25% of the value in one structure plus 75% of the value in the other structure. The profile provided by three different basis sets are shown in Fig. 2. In each instance the cyclic ion is found to be much more stable than the open cation but the computed difference decreases as the size of the basis set is increased, as is usual for energy differences computed by the molecular orbital method. All the profiles show small activation energies going from the open cation to the cyclic one but, as no attempt was made to obtain a surface for this reaction, then the maximum on the profiles must be considered as upper estimates for the activated complexes.

Aziridines readily undergo ring opening in the presence of halogen acids and the mechanism of this reaction has been established to be an S_N2 displacement reaction at a carbon atom. In early work the mechanism was postulated to involve protonated aziridine in equilibrium with the 2-aminoethyl cation [49], but recently it has been established that this equilibrium does not exist and that the reaction involves the bimolecular mechanism described above [50]. Our reaction profiles (Fig. 2) indicate that the 2-aminoethyl cation is too unstable to exist even as a transient intermediate in the hydrolysis of the aziridine, in complete agreement with the most recent results from solution chemistry.



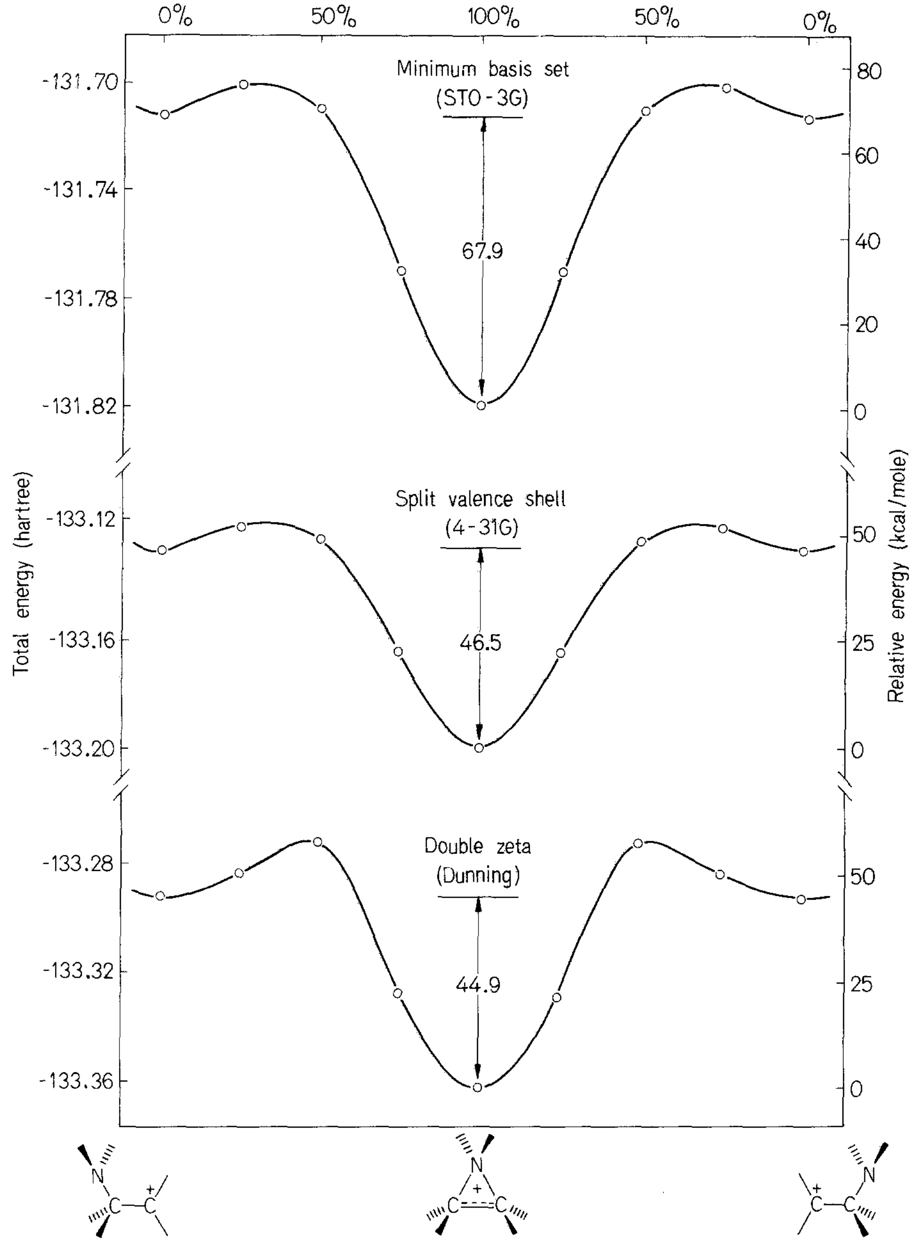


Fig. 2. Profile for interconversion of the 2-aminoethyl and aziridinium cations with the STO-3G, 4-31G and double-zeta basis sets

3.4. Dependence of Cyclic versus Open Cations on Heteroatoms

As described briefly in the introduction, the profiles to interconversion of open and cyclic $XC_2H_4^+$ cations have been computed previously [9, 10, 14, 15] using this same double-zeta basis set (Fig. 3 and Table 3). For each heteroatom *both* the cyclic non-classical and the classical 2-heteroethyl cations are computed to exist at

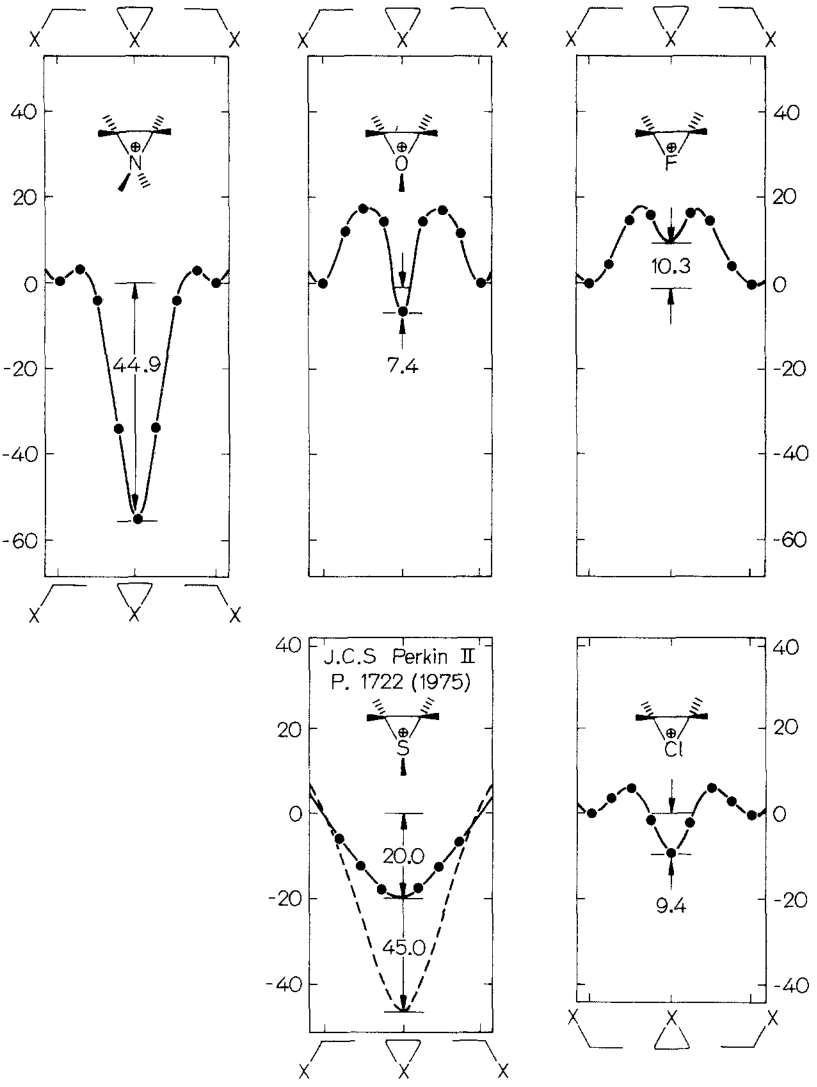
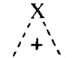
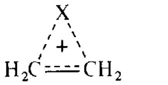


Fig. 3. Profile for interconversion of 2-hetero-ethyl cations, $XCH_2CH_2^+$, and the bridged ions  $H_2C\overset{X}{\overset{+}{=\!=}}CH_2$ for X = NH_2, OH, F, SH and Cl. The profiles were all computed using the double-zeta basis set except for the one involving sulphur, where the smaller 4-31G basis set was used

minima on the $C_2H_4X^+$ surfaces. When X is F the cyclic ion is the less stable but for X = Cl, OH and NH_2 the cyclic ions are the more stable. The amino group is by far the most effective bridging substituent.

The trend noted previously for heteroatoms in the same row of the periodic table, namely that the softer elements in group 6 are more effective at bridging than those

Table 3. Energy difference (kcal/mole) between



$\overset{\overset{X}{+}}{H_2C{=}CH_2}$

and $XCH_2CH_2^+$ as computed by 4-31G and $(9^s5^p/4^s) \rightarrow [4^s2^p/2^s]$ basis sets[a]

Substituent	4-31G	$(9^s5^p/4^s) \rightarrow [4^s2^p/2^s]$
NH_2	46.5	44.9
OH	9.1	7.2
F	−7.4[b]	−10.3
SH	20	45[c]
Cl	−11.7	−9.4

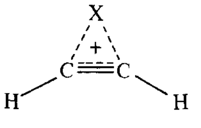
[a] Positive energy indicates cyclic ion is the more stable.

[b] Result from 6-31G basis set calculations.

[c] Estimated

in group 7 of the same row, is shown to be continued down into group 5. Clearly there is a greater tendency towards bridging for the larger second-row elements but nitrogen is computed to be a more effective atom for bridging than chlorine and is comparable to sulphur (note that the sulphur calculations employed a smaller basis set (4-31G) and comparisons are therefore more difficult). One of the reasons for the apparent stability of the cyclic ions is, in fact, the high instability of the open cations, which are primary carbenium ions stabilized only by hyperconjugation from the CH_2X group to the carbenium ion centre. Substitution of one of the hydrogens by an alkyl group results in the open cation (now a secondary carbenium ion) being more stable and bridging is less important. [51]

In electrophilic additions to acetylenes there is also the possibility of open or cyclic cations, but in this case the open vinyl cations, $XCH{=}CH^+$, are found to be more stable experimentally then the primary carbenium ions, $XCH_2CH_2^+$, formed in the addition to double bonds. In fact, using the same double-zeta basis set as in the current work for X = F and Cl, the bridged ions,



are computed not to be at minima on the reaction surfaces and only for X = SH and NH_2 are the cyclic ions computed to be more stable than their open isomers [18–22]. Furthermore the ability of substituents to stabilize the cyclic ion relative to the open cation is always computed to be larger for the $C_2H_4X^+$ ions than for the $C_2H_2X^+$ ions. The relative abilities of the different hetero-substituents to stabilize the cyclic ions is $NH_2 > SH > OH > Cl > F$ for the $C_2H_2X^+$ system and $NH_2 > SH > Cl \approx OH > F$ for $C_2H_4X^+$.

All these profiles to interconversion suffer from the same theoretical deficiencies, namely that inclusion of polarization functions (*p*-functions on H and *d*-functions on C and on the heteroatoms) have not been included in constructing the double-zeta wavefunctions and that correlation energy effects have been assumed either to be negligible or to cancel when comparing ions with the same number of electron pairs. Extended basis set Hartree–Fock calculations on $C_2H_5^+$ and on $C_2H_3^+$ have established that polarization functions improve the energies of the non-classical cations more than those of the classical cations. Thus for $C_2H_5^+$ both the open and cyclic ions are computed to have the same energy with the 6-31G** basis set [48] while the cyclic ion is computed to be the more stable for $C_2H_3^+$ when using a $(7^s3^p1^d; 3^s1^p)$ basis set [16]. Inclusion of correlation energy also has been shown to improve the energy of the cyclic ions relative to the open cations [16, 48, 52–54]. Clearly then further refinement of the double-zeta basis set calculations presented in this work either by inclusion of polarization functions or by configuration interaction calculations can be expected to further stabilize the cyclic ion relative to the open one. We therefore believe that for qualitative comparisons the reaction profiles given in Fig. 3 satisfactorily represent the relative abilities of the different heteroatoms to bridge two carbon atoms effectively.

3.5. Gas Phase Dissociation of β-Heteroethanols

Caserio and co-workers [55] have examined the protonation and subsequent dissociation of a series of β-heteroethanols, XH_2CCH_2OH, in the gas phase. In principle either HX or water will be eliminated along with formation of a $C_2H_4OH^+$ or $C_2H_4X^+$ species. Molecular orbital calculations are for the reaction of isolated molecules in the gas phase and should therefore be in agreement with these experimental results. From our double-zeta calculations we were able to calculate the relative energies of the two possible pairs of products for X = NH_2, F, Cl. The computed energy differences are given in Table 4. For X = NH_2 the computed negative energy for the reaction is consistent with the experimental observation that only $C_2H_4NH_3^+$ and no $C_2H_4OH^+$ is produced from protonated β-amino ethanol. For X = F and Cl the computed positive energies suggest that only $C_2H_4OH^+$ and no $C_2H_4X^+$ should be formed from β-haloethanols. However experiment has shown

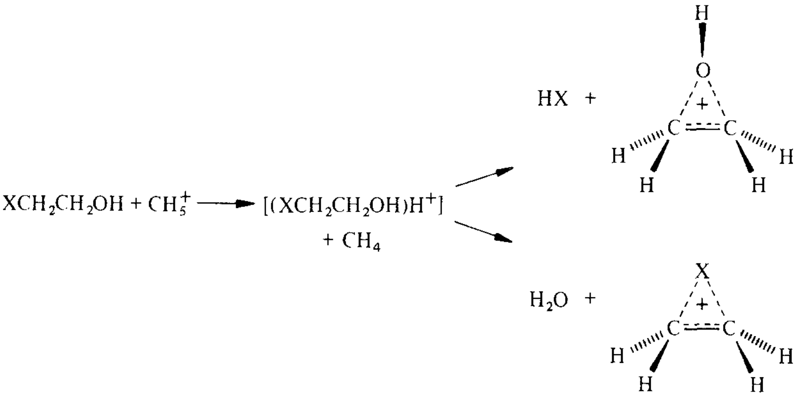
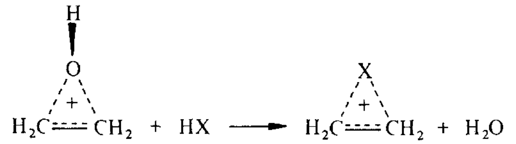


Table 4. Change in energy (kcal/mole) for the reaction



as calculated from the double-zeta basis set calculations[a]

Substituent	Energy difference
NH_2	−21.2[b]
F	49.6[c]
Cl	23.3[d]

[a] Double-zeta energy for H_2O, −76.0093, taken from Ref. [37].

[b] Double-zeta energy for NH_3, −51.18027 hartree, taken from A. C. Hopkinson and M. H. Lien, Intern. J. Quantum Chem. **13**, 349 (1978).

[c] Double-zeta energy for HF computed to be −100.02197 hartree.

[d] Double-zeta energy for HCl computed to be −460.04644 hartree.

that roughly equal amounts of *both* ions are produced by *both* haloethanols. We tentatively suggest that this discrepancy can be explained by the eventual product of dissociation being determined, in part, by the initial site of protonation and not totally by the thermodynamic stabilities of the possible products. Protonation at oxygen occurs more readily than at chlorine and fluorine (relative proton affinities for C_2H_5OH, C_2H_5Cl and C_2H_5F are 186 [56], 167 [57] and 163 [57] kcal/mole respectively) and loss of water from $XCH_2CH_2OH_2^+$ is simple to envisage mechanistically. Generation of the thermodynamically more stable products, halogen acid and the cyclic $C_2H_4OH^+$ ion, however, requires protonation at the energetically much less accessible halogen atom and this could only be achieved in the initial proton transfer from CH_5^+ or by an intramolecular 1,4-shift in the excited hydroxy-protonated isomer. There is some precedent for the postulation of protonated organic bases dissociating into the thermodynamically less stable products. Recent gas phase studies [58] have established that when formic acid is protonated by a series of Brønsted acids of varying strengths then it dissociates by simple carbon-oxygen fission to yield H_2O and HCO^+, rather than to form the thermodynamically more stable CO and H_3O^+.

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