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Quantum Chemical Studies on Electrophilic Addition

III. Reaction of Hydroxonium Ion with Ethylene. Acid Catalysed Ring Opening of Epoxides

Alan C. Hopkinson, Min H. Lien

Department of Chemistry, York University, 4700 Keele Street, Downsview, Ontario M3J 1P3, Canada

Imre G. Csizmadia, Keith Yates

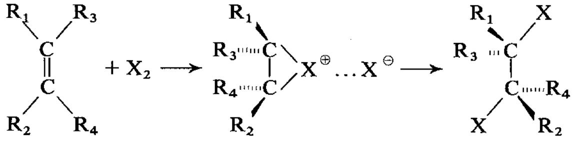
Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 1A1, Canada

The geometries of the 2-hydroxyethyl and isomeric oxiranium cations have been fully optimized using *ab initio* molecular orbital calculations employing the split valence shell 4-31G basis set. These species are possible intermediates in both the electrophilic addition of $OH^{\oplus}$ to ethylene and in the acid catalysed ring opening of oxirane. The optimized structures were then used to compute more accurate wave functions using Dunning's double-zeta basis set, and with this large basis set the bridged oxiranium ion was found to be the more stable by 7.2 kcal/mole. The barrier to interconversion of these two $C_2H_4OH^{\oplus}$ ions was computed to be 25.0 kcal/mole above the oxiranium ion.

Key words: Hydroxonium ion, reaction of ~ with ethylene – Epoxides, acid catalysed ring opening of ~

1. Introduction

Halogenation is a classic example of electrophilic addition to a double bond. In this reaction the halogen molecule is polarized by the π-system of the alkene and the hypothetical $X^{\oplus}$ion is added to the double bond, initially forming a bridged halonium ion [1–3]. Peroxyacid oxidation of alkenes to epoxides are normally considered to follow a rather different mechanism referred to as the "butterfly" mechanism [4]. Here the proton of the peroxyacid is transferred to the carbonyl oxygen at the same time as the oxygen atom is added to the double bond and the



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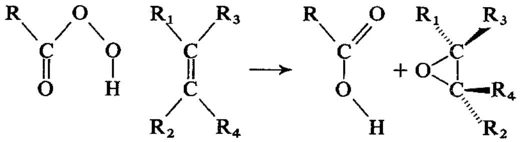
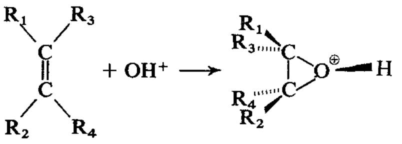


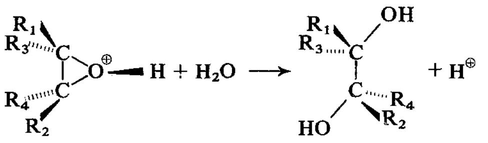
(2)

products of the reaction are the epoxide and carboxylic acid. However it is possible that in polar solvents the reaction is initiated by formation of $OH^{\oplus}$, produced by the breakdown of the peroxyacid, and the epoxidation could then be considered as the combination of $OH^{\oplus}$ and the alkene.



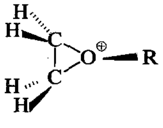
(3)

The protonated epoxide or oxiranium ion, formed in Eq. (3) as an intermediate in the electrophilic addition to the double bond, is also an intermediate in the acid catalysed ring opening of epoxides. The mechanism of this reaction has been shown to be A2, i.e. attack of the nucleophile (usually water) on the oxiranium ion [5–7]. This reaction occurs in dilute acid and this remarkable sensitivity of an ether to acid catalysed hydrolysis is attributed to the loss of a large amount of strain on opening of the three-membered ring.



(4)

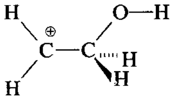
Several O-alkyloxiranium cations (I, $R = CH_3-$, C_2H_5- and $(CH_3)_2CH-$) have been produced by alkylation of oxirane in solvents of low nucleophilicity [8–11].



I

At −70°C the ring methylene protons give different NMR signals characteristic of protons in *cis* and *trans* positions relative to the substituent R. This implies that the geometry about the oxygen is pyramidal and, as the signals coalesce at −50°C ($R = (CH_3)_2CH-$), the barrier to inversion is small [8].

Our interest in ions of type I stems from our theoretical studies on the ring opening of the cyclic $C_2H_4F^{\oplus}$ and $C_2H_4Cl^{\oplus}$ ions [12, 13], species which are models for the intermediates in halogenation of alkenes. The present work, in which we examine the oxiranium ion (I, $R = H$) and the 2-hydroxyethyl cation (II), is a natural continuation of this series.



II

2. Computational Details

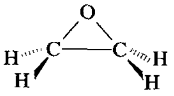
Single determinant non-empirical SCF-MO calculations were used throughout this study. The geometry optimizations for the 2-hydroxyethyl and oxiranium cations required many calculations and for this we employed the split-valence shell 4-31G basis set [14, 15] in the GAUSSIAN 70 program [16]. Near Hartree-Fock wave functions were then computed using Dunning's [17] double-zeta basis set with a modified [18] POLYATOM II program [19].

The calculations were carried out on the York University IBM 370/155 and University of Toronto IBM 370/165 computers.

3. Results and Discussion

3.1. *Geometry Optimization*

Relatively few experimental geometries are available in the literature for organic cations and it was difficult to make an "educated guess" at the geometries of the $C_2H_4OH^{\oplus}$ ions I and II. We therefore decided to fully optimize the geometries of these two ions using the 4-31G basis set and the optimization procedure built into the GAUSSIAN 70 program [16]. As a test of the validity of this basis set for geometry optimization we first examined the closely related oxirane molecule (III)



III

and compared the experimental (from microwave data [20]) and computed geometries. The agreement between experiment and theory, shown in Fig. 1 is very

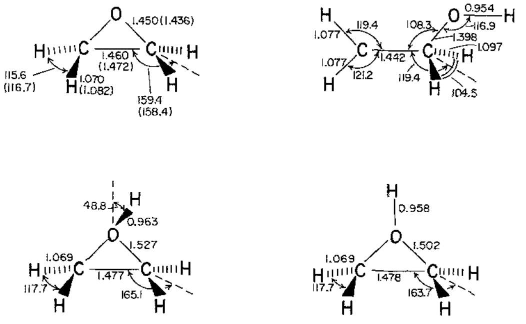


Fig. 1. Computed optimum geometries for oxirane, 2-hydroxyethyl cation and the oxiranium ion (both planar and pyramidal). Bond lengths are in Å and angles are in degrees. Bracketed values for oxirane are those taken from microwave measurements (Ref. [20])

good, although the smaller STO-3G basis set [21, 22] calculation [23] gives bond lengths slightly closer to the experimental value. However the geometry from the 4-31G calculations appears to be the best for molecular orbital purposes as the more accurate double-zeta basis set calculations gave a better energy (by 0.43 kcal/mole) using the 4-31G geometry than with the experimental one. It therefore seems that optimization with the 4-31G basis set gives satisfactory molecular structures and we used this basis set to optimize geometries for the two cations.

Preliminary studies on the 2-hydroxyethyl cation (II) showed the two hydrogen atoms of the methylene group to be coplanar with the oxygen atom, and the hydrogen of the hydroxy group to also be in this plane in the *s-trans* conformation relative to the C–C bond. A similar study on the oxiranium ion (I) showed the geometry about the oxygen atom to be pyramidal, in agreement with experimental observation.

These optimum conformations were then subjected to the usual GAUSSIAN 70 optimization procedure, varying each parameter in turn starting with the bonds involving the heavier atoms. This sequence was repeated until optimum geometries were obtained and the results are given in Fig. 1.

Comparison of the geometries of the oxiranium ion (I) and oxirane (III) shows that on protonation there is very little difference in both the C–C and C–H bond lengths but that there is a considerable increase (0.077 Å) in the C–O distance.

The 2-hydroxyethyl cation (II) has considerably shorter C–C and C–O bond lengths than those reported for ethanol (1.533 and 1.420 Å respectively [24]) and this may be attributed to conjugative delocalization of the oxygen lone pair onto the electron deficient carbon.

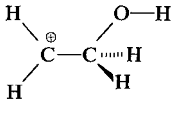
3.2. Details of the Double-Zeta Basis Set Calculations

The optimum structures produced by the 4-31G basis set calculations were used to obtain wave functions with the larger Dunning basis set (9^s5^p; 4^s contracted to 4^s2^p; 2^s [17]). The details of these larger basis set calculations, along with the energy from the 4-31G basis set calculations, are given in Table 1 and the net charges computed with the double zeta calculations are given in Fig. 2.

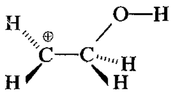
3.3. Conformational Preferences in 2-Hydroxyethyl Cation

3.3.1. Methylene Group

There are two possible conformations for the planar CH$_2^{\oplus}$ group in the 2-hydroxyethyl cation, one in which the oxygen and this group are coplanar (IV, eclipsed) and

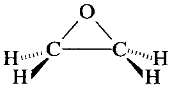
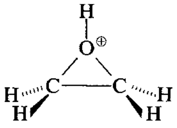
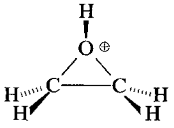
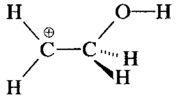


IV



V

Table 1. Total energy, orbital energies (hartree) and virial coefficients for oxirane, oxiranium and 2-hydroxyethyl cations from Dunning basis set calculations

Molecule				
Point group	C_{2v}	C_{2v}	C_s	C_s
Orbital energies	$-20.5659\ (1a_1)$ $-11.2960\ (2a_1)$ $-11.2952\ (1b_1)$ $-\ 1.4129\ (3a_1)$ $-\ 0.9491\ (4a_1)$ $-\ 0.8724\ (2b_1)$ $-\ 0.7174\ (1b_2)$ $-\ 0.6564\ (5a_1)$ $-\ 0.5546\ (1a_2)$ $-\ 0.5312\ (3b_1)$ $-\ 0.4579\ (6a_1)$ $-\ 0.4540\ (2b_2)$	$-20.8631\ (1a_1)$ $-11.5726\ (2a_1)$ $-11.5719\ (1b_1)$ $-\ 1.7034\ (3a_1)$ $-\ 1.3008\ (4a_1)$ $-\ 1.1262\ (2b_1)$ $-\ 0.9999\ (5a_1)$ $-\ 0.9766\ (1b_2)$ $-\ 0.8302\ (3b_1)$ $-\ 0.8057\ (1a_2)$ $-\ 0.7940\ (6a_1)$ $-\ 0.7686\ (2b_2)$	$-20.8862\ (1a')$ $-11.5743\ (2a')$ $-11.5736\ (1a'')$ $-\ 1.7219\ (3a')$ $-\ 1.2959\ (4a')$ $-\ 1.1319\ (2a'')$ $-\ 1.0182\ (5a')$ $-\ 0.9554\ (6a')$ $-\ 0.8350\ (3a'')$ $-\ 0.8321\ (7a')$ $-\ 0.8121\ (4a'')$ $-\ 0.7625\ (8a')$	$-20.7657\ (1a')$ $-11.6351\ (2a')$ $-11.5524\ (3a')$ $-\ 1.5983\ (4a')$ $-\ 1.3287\ (5a')$ $-\ 1.1137\ (6a')$ $-\ 0.9844\ (7a')$ $-\ 0.8857\ (1a'')$ $-\ 0.8787\ (8a')$ $-\ 0.8679\ (9a')$ $-\ 0.7320\ (10a')$ $-\ 0.6775\ (2a'')$
Total energy	-152.81183	-153.12059	-153.12934	-153.11780
Virial coefficient	1.99861	1.99856	1.99858	1.99872
Total energy from 4-31G basis set	-152.62669	-152.93831	-152.94538	-152.93088

the other having the oxygen atom and the empty p-orbital of the carbonium ion centre coplanar (V bisected). In the ethyl cation (OH of IV replaced by H) there is only a very small rotational barrier but introduction of a substituent of greater electronegativity than hydrogen at the β carbon produces a much larger two-fold barrier with the eclipsed form being the more stable [25–28]. The origin of this barrier lies in the interaction of the formally empty p-orbital of the carbonium ion interacting with orbitals of the same symmetry on the adjacent saturated carbon atom. In the bisected conformation this p-orbital lies in the same plane as the C–O bond (structure VI) and withdraws electron density from this bond. However the

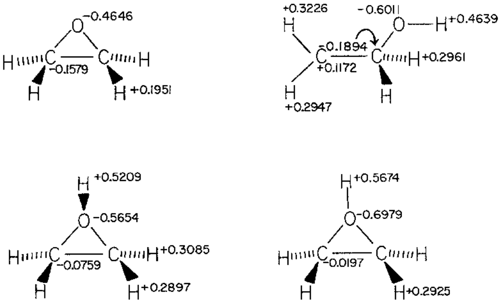
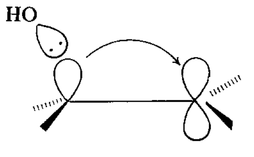
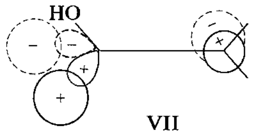


Fig. 2. Net-charges for oxirane, 2-hydroxyethyl cation and the oxiranium ion (both planar and pyramidal) as computed with the Dunning basis set



VI



VII

polarization of this bond caused by the high electronegativity of the oxygen atom makes this an unfavourable interaction. In the eclipsed form (structure VII) the empty *p*-orbital interacts with the appropriate π-component of the two hydrogen atoms and since hydrogen is less electronegative than oxygen, electron density is more available from this interaction and this then is the preferred conformation.

We examined the barrier to rotation of this CH_2 group using the Dunning basis set and obtained a profile (shown in Fig. 3) of the type predicted by the theory. The

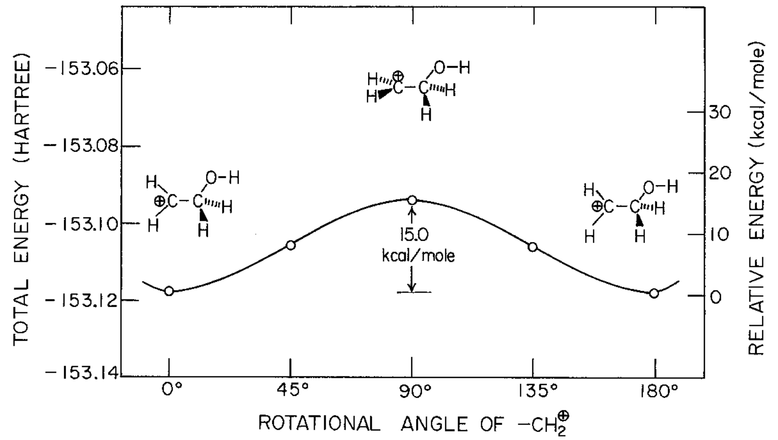


Fig. 3. Profile for rotation of planar $CH_2^{\oplus}$ group in the 2-hydroxyethyl cation, as computed by the Dunning basis set

computed barrier of 15.0 kcal/mole is slightly less than that of the 2-fluoroethyl cation (17.6 kcal/mole [12]) but is considerably larger than for the 2-chloroethyl cation (6.5 kcal/mole [13]). The relative magnitudes of these rotational barriers poses some problems in terms of a model based purely on electronegativity arguments, as oxygen is generally accepted as being close to chlorine and considerably less electronegative than fluorine. Examination of the geometries revealed that the CCX angle in the 2-hydroxyethyl cation (108.3°) is slightly less than the ideal tetrahedral angle whereas those of the 2-chloro- and 2-fluoroethyl cations (114.2° and 112.1° respectively) are larger. Furthermore the CCH angle for the proton of the methylene group eclipsing the heteroatom (119.6°) is also slightly less than the ideal angle of 120°, whereas in the 2-chloro- and 2-fluoroethyl cations these angles are slightly larger (120.8° and 121.7°). These slight structural differences suggest that in the eclipsed conformation there is a weak attraction between the group X and the methylene proton and this is largest when X is oxygen. This argument is

Table 2. Comparison of computed X–H distance in 2 X-ethyl cations with van der Waals radii (distances in Å)

Substituent	Computed X–H	Sum of Van der Waals radii[a]
Oxygen	2.439	2.60
Fluorine	2.520	2.55
Chlorine	2.860	3.00

[a] Ref. [29].

reinforced by comparing the distances between X and the methylene proton with the van der Waals radii for non-bonded atoms [29] (Table 2). The computed distances between oxygen and hydrogen, and chlorine and hydrogen are both shorter than the van der Waals radii by about 0.15 Å. However the computed F···H distance is the same as the van der Waals radii indicating that the fluorine does not significantly interact with the acidic methylene proton and this can be attributed to the lone pairs of fluorine being more tightly bound.

3.3.2. Hydroxy Group

The proton of the hydroxy group in the optimum structure of the 2-hydroxyethyl cation is in an *s-trans* conformation relative to the C–C bond. This is the most acidic proton in the ion and by adopting this conformation it is at a maximum distance from the electron deficient carbon, thereby minimizing the interaction between two positively charged atoms.

3.4. Inversion Barrier in the Oxiranium Cation

As outlined in the introduction, O-alkyloxiranium cations are pyramidal about the oxygen atom but have low inversion barriers [8]. Our *ab initio* calculations also showed the oxygen to be pyramidal, with the proton being 48° out of the COC plane. We reoptimized the structure of the oxiranium ion with the geometry about the oxygen being planar. The optimum geometries for the planar and non-planar structures are very similar with the most pronounced difference being a shorter C–O distance (by 0.025 Å) in the planar ion. The computed barrier to inversion was 4.4 kcal/mole (4-31G) and 5.5 kcal/mole (Dunning basis set) and, as energy differences are normally overestimated by molecular orbital calculations, it is probable that the actual barrier is somewhat smaller. This compares with an experimental value of 10 kcal/mole for the O-isopropyloxiranium ion [8]. The computed barrier differs markedly from the minimum basis set results on the thiiranium ion, $C_2H_4SH^{\oplus}$, where an inversion barrier of 78.1 kcal/mole was calculated [30]. A similar increase in an inversion barrier on replacing oxygen with sulphur (17.1 to 74.0 kcal/mole) has been found for the symmetrically bridged $C_2H_2XH^{\oplus}$ ions [31].

3.5. Protonation of Oxirane

Protonation of oxirane causes considerable lengthening of the C–O bond (0.077 Å), a slight lengthening of the C–C bond (0.017 Å), and very little difference in the methylene groups. All the positive charge of the oxonium ion is on the hydrogen atoms, as is usual in organic cations. The oxygen atoms in both oxirane and the oxiranium cation carry large negative charges, although in the cation the oxygen formally carries a positive charge. Indeed protonation of oxirane actually increases the negative charge on the oxygen, while the carbon atoms in the ion have less negative charge than in oxirane. This latter feature should facilitate the attack of nucleophiles on the carbon atoms of the three-membered ring and this is consistent with the experimental observation that acid-catalysed ring opening of epoxides occurs by the A2 process [5–7].

The protonation of oxirane increases the binding energies of *all* the electrons, the inner orbitals being changed by about the same amount as the valence orbitals (Table 1). The simplest comparison is between the planar oxiranium cation and oxirane as both belong to the C_{2v} point group. Addition of the proton to the oxygen increases the number of functions belonging to the a_1 irreducible representation and the molecular orbitals of this symmetry are correspondingly stabilized the most. The a_1 orbitals in the valence shell are stabilized by about 0.34 hartree while all the other orbitals change by about 0.28 hartree. In its equilibrium non-planar geometry the oxiranium ion belongs to the C_s point group and the a_1 and b_2 irreducible representations of the C_{2v} point group become a', while a_2 and b_1 become a''.

3.6. Profile for Interconversion of Open and Cyclic Ions

If in a polar solvent peroxyacids add $OH^{\oplus}$ to an alkene then the initial intermediate formed would be the oxiranium ion. This ion is also the initial intermediate in the acid-catalysed ring opening of oxirane. The subsequent reaction of this ion could then involve a nucleophile as in the A2 ring opening reaction or, in the absence of a good nucleophile, could conceivably be unimolecular ring opening to form the 2-hydroxyethyl cation. The interconversion of cyclic and open cations has been of considerable interest recently and we have therefore computed a reaction profile for the interconversion of the oxiranium and 2-hydroxyethyl cations. We have examined intermediate structures between the ions, assuming that the motions of all the atoms occur in a synchronized fashion. The results of this study, with all three basis sets (Fig. 4), show the existence of a transition state a considerable height above the oxiranium ion. The lowest barrier (25 kcal/mole) is predicted with the largest (and therefore most reliable) basis set and, as improvement of the wave function by inclusion of polarization functions on the bridging atom [32] and by using configuration interaction [33] will both probably result in further stabilization of the bridged ion, this is probably an underestimation of the barrier. These calculations then suggest that ring opening of the oxiranium ion will not be a facile process at room temperature and this is consistent with the experimental observation that the acid-catalysed hydration of oxirane is by the A2 mechanism [5, 6] (involving the attack of water on the oxiranium ion with

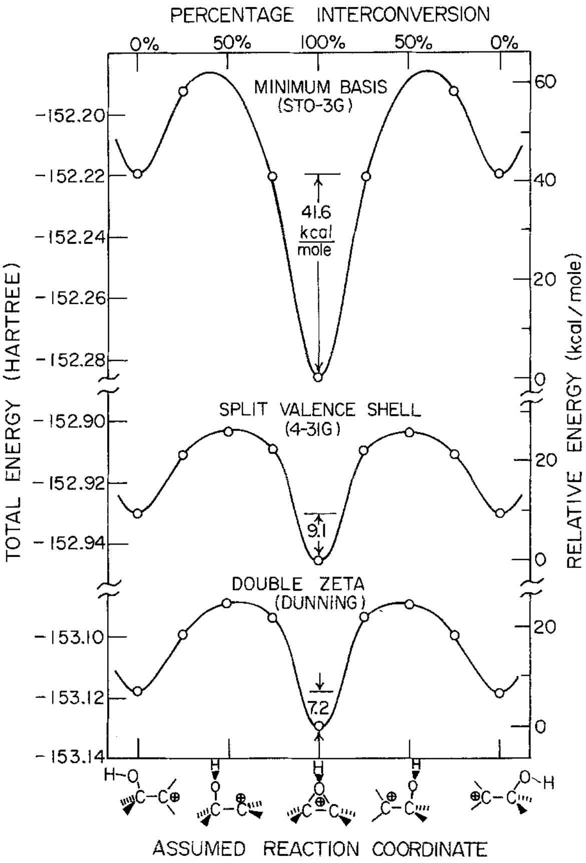
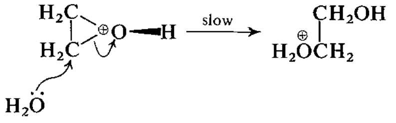
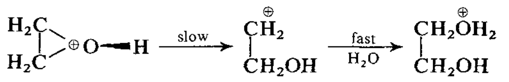


Fig. 4. Profile for interconversion of 2-hydroxyethyl and oxiranium cations with three different basis sets

synchronous ring opening) and not the unimolecular ring opening reaction (A1)



A2 process



A1 process

Partitioning of the total energy into its electronic (attractive) and nuclear repulsion components [34–36] shows that proceeding from the oxiranium ion the barrier to interconversion is caused by the electronic energy decreasing faster than the simultaneous decrease in the nuclear repulsion energy (Fig. 5). However as both the electronic and nuclear repulsion energies show monotonic decreases in going from the oxiranium ion to the 2-hydroxyethyl cation then the maximum on the total energy profile corresponds to the point at which these two are decreasing

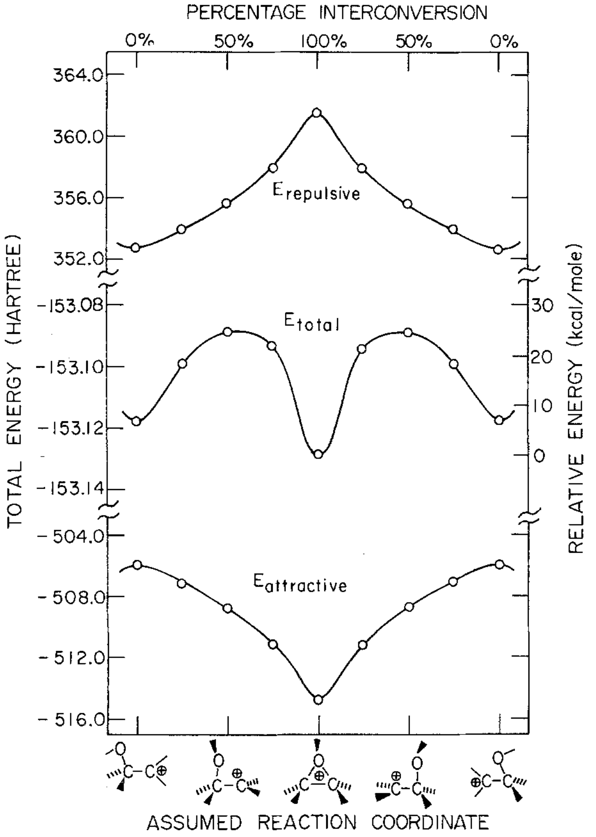


Fig. 5. The partitioning of the total energy (Dunning basis set) for the reaction profile into repulsive and attractive components

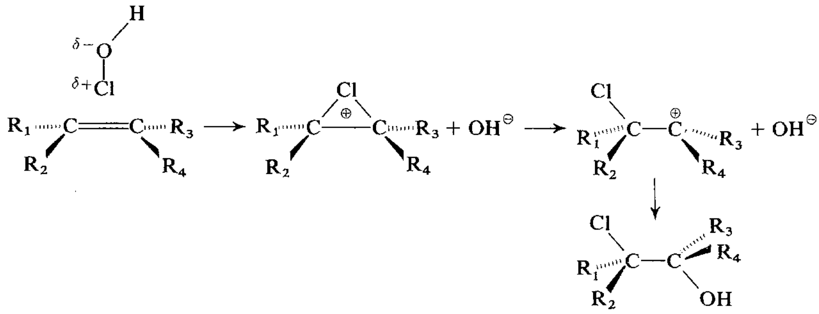
at the same rate. On the 2-hydroxyethyl side of the maximum the decrease in nuclear repulsion must be greater than that in the electronic energy. This type of behaviour has been observed previously for the interconversion of the thiiranium and 2-thioethyl cations.

The overall shape of the reaction profile for interconversion of the two $C_2H_4OH^\oplus$ ions is similar to that found for the $C_2H_4Cl^\oplus$ systems [13], although in this latter case the barrier is smaller (15.6 kcal/mole as opposed to 25 kcal/mole). By contrast the profile for interconversion of $C_2H_4SH^\oplus$ ions has a maximum at the 2-thioethyl cation, i.e. this ion spontaneously collapses to the cyclic thiiranium ion [30]. Furthermore, the profile for the isoelectronic $C_2H_4F^\oplus$ system has the 2-fluoroethyl cation more stable than cyclic fluoronium ion with a barrier of only 8.5 kcal/mole [12].

It is apparent from the different profiles that the bridged ion becomes increasingly more stable relative to its open tautomer as the size of the atom is increased (i.e. on going from an element in the first row to the second row of the periodic table). Also an element in group 6 is a more effective bridging atom than the group 7 element adjacent to it in the periodic table. This property can be attributed to the larger nuclear charge on the halogen atom resulting in more tightly bound, and therefore less available, valence electrons.

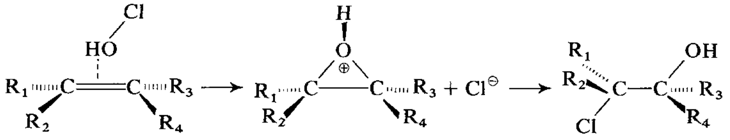
3.7. *Addition of Hypochlorous Acid to Alkenes*

The mechanism of addition of hypochlorous acid to an alkene in solution is electrophilic with the initial attack by the slightly positively charged chlorine [37]. In accordance with Markovnikov's rule, when the alkene contains alkyl or aryl substituents then the chlorine adds to the less substituted carbon atom. This would form the more stable open carbonium ion and subsequent reaction with either a hydroxyl ion or water results in formation of the chlorohydrin. The addition occurs with *trans* stereochemistry [37], suggesting that the intermediate carbonium ion which reacts with the nucleophile is best described as an *unsymmetrically bridged* alkenechloronium cation and not as a 2-chloroalkyl cation. However in several studies [38–41] significant amounts of the anti-Markovnikov product have been observed and there appears to have been no definitive study on the mechanism of hypochlorous acid to alkenes.



Scheme 1

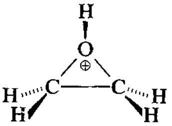
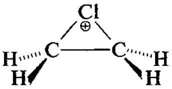
The addition of sulphenyl halides to alkenes, unlike the hypochlorous acid addition described above, proceeds by electrophilic attack of SR$^{\oplus}$ on the alkene and forms the thiiranium cation as an intermediate. In a similar manner formation of the chlorohydrin could also involve the protonated epoxide as an intermediate. Both oxygen and chlorine have similar electronegativities and this pathway appears to be a feasible alternative to the generally accepted mechanism.



Scheme 2

Comparison of the energies of the intermediates in Schemes 1 and 2, as computed with the Dunning basis set, should predict which of these mechanisms is the more probable for the gas phase reaction.[1] The energies from the appropriate calculations are reported in Table 3 and from this data the oxiranium ion pathway is predicted to be favoured by 87.6 kcal/mole. This energy difference is too large to attribute to deficiencies in the basis set and, since the comparison involves ions of similar structure with the same number of bonds in each pair of intermediates, then the neglect of correlation energy resulting from the use of near Hartree-Fock molecular orbitals is also not responsible for the energy difference. It therefore seems that the electrophilic addition of hypochlorous acid to ethylene in the gas phase follows a different mechanism from that generally accepted for the solution reaction.

Table 3. Dunning basis set calculations on possible intermediates in electrophilic addition of hypochlorous acid to ethylene

Ion	Energy (hartree)
$Cl^{\ominus}$	−459.51591
$OH^{\ominus}$	−75.34543
	−153.12934
	−537.16027

The solvation energy of all the ions is expected to be large but it is not obvious that the ethylenechloronium and hydroxyl ions will be stabilized by a much larger amount than the oxiranium and chloride ions. It therefore seems possible that even in the solution reaction the hydroxy-bridged ion is the initially formed intermediate. According to our calculations this is unlikely to ring open in a unimolecular reaction and nucleophilic attack by the large chloride ion on the bridged cation would be most probable at the less sterically hindered (i.e. *less substituted*) carbon atom. This mechanism would then accommodate both the larger intrinsic stability of the hydroxy-bridged cation and also the observed Markovnikov product.

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[1] Ionic reactions between neutral molecules in the gas phase are rare and the reaction between ethylene and hypochlorous acid is more likely to occur via a radical mechanism.

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