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Valence Isomerization of Ionized Oxirane

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Abstract: The valence isomerization reactions of the cation radical of oxirane are investigated using *ab initio* QCISD methods. There are two stable forms of the ion with the ring intact. The O ionized form is the ground state; a C-C ionized state lies 10.0 kJ/mol higher. The activation energy for ring opening is 23.2 kJ/mol. The open form is planar, has C_{2v} symmetry, and is 99.7 kJ/mol more stable than the ground state with the ring intact. IRC calculations at the MP2 level follow the reaction from both the conrotatory and disrotatory transition states.

Ever since Woodward and Hoffmann published their predictions concerning the stereoelectronic course of electrocyclic reactions in 1965, it has been obvious that the arguments are less compelling for species containing an odd number of electrons.[1] This is particularly clear in the Longuet-Higgins treatment of the cyclopropyl radical.[2] In that case neither conrotatory nor disrotatory ring opening is strictly allowed. The implications are twofold: Ring opening of cyclic radicals should have an associated activation energy, and there may be no strong preference for either conrotatory or disrotatory opening. Dewar and Kirschner used semiempirical methods to predict that the ring opening of the cyclopropyl radical occurs by an unsymmetrical path preserving neither the C_s plane of symmetry of the disrotatory process nor the twofold (C_2) axis of symmetry of the conrotatory process in the transition state (TS).[3] Olivella, Sole, and Bofill extended this line of reasoning with *ab initio* methods.[4] In agreement with Dewar and Kirschner[3] they found that the TS was unsymmetrical. Besides locating the TS, they followed the course of the reaction with intrinsic reaction coordinate (IRC) calculations. The reaction occurs in two stages. In the first stage the ring opens up and one methylene rotates into planarity with the carbons. Then the other methylene rotates into planarity in the second stage. The cation radical of oxirane ($EO^{+\cdot}$) is isoelectronic with the cyclopropyl radical. It is of interest to determine if orbital symmetry plays a role in the electrocyclic reaction of $EO^{+\cdot}$.

A brief review of the nomenclature of symmetry designations as applied to $EO^{+\cdot}$ will facilitate an understanding of the following text. $EO^{+\cdot}$ belongs to the point group C_{2v}, which has a C_2 axis of symmetry as well as a plane of symmetry (σ_v) containing the C_2 axis. The orbitals of a system with C_{2v} symmetry, if nondegenerate, are either symmetrical or antisymmetrical with respect to the C_2 axis and σ_v. Those that are symmetrical with respect to C_2 are designated a while those that are antisymmetrical are b. Symmetry with respect to σ_v is designated by subscripts: 1 for symmetric orbitals and 2 for antisymmetric ones. Electronic states are designated with capital letters. States with only one singly occupied MO (SOMO) have the same symmetry as the SOMO they contain. In some of the structures we found, the molecule has lost the C_2 axis, but retains the σ_v, which is perpendicular to the plane of the heavy atoms. Such structures are said to have C_s symmetry. The nondegenerate orbitals of C_s symmetry are classified as a′ or a″ according to whether they are

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symmetrical or antisymmetrical, respectively. All of the electronic states considered in this work have only one SOMO, and we encountered no orbital degeneracies.

An early study by Bouma, MacLeod, and Radom of $EO^{+\cdot}$ found the ground state to be the O ionized $^2B_1$ state. As they increased the COC bond angle, a C-C ionized $^2A'$ state became the lowest energy one. Their study predicted an activation energy of about 110 kJ/mol for ring opening of the C-C bond.[5] This figure was derived by constraining the system to a plane of symmetry as the COC bond angle was increased. There are several reasons to doubt the wisdom of enforcing this plane of symmetry (which may have been dictated by the limited computational capacity of that time), some of them provided by the authors themselves. Firstly, they concluded that the ring-opened form of the oxirane ion has no plane of symmetry perpendicular to the plane of the heavy atoms. Consequently their work indicates that the plane of symmetry must be abandoned at some point in the electrocyclic reaction. Secondly, they noted that, as the C-C bond is lengthened, a $^2A'$ state of C_{2v} geometry becomes the most stable one. However, from such a state (representing C-C ionization) the conrotatory process (which preserves a C_2 axis rather than a plane of symmetry) is orbital-symmetry allowed:

σ^* (A) ——	ψ_3 (A) ——
σ (S) ↑	ψ_2 (S) ↑
O2p (A) ↑↓	ψ_1 (A) ↑↓

There is no correspondingly allowed disrotatory process from either the $^2B_1$ or $^2A_1$ states of $EO^{+\cdot}$ because both occupied orbitals are symmetric with respect to the plane of symmetry in the ring-intact ion, and one of them must transform into the allyl type ψ_2 which is antisymmetric. We supposed that any transition states for this reaction would be lower in energy than suggested in the previous study and have either an axis of symmetry (by the orbital symmetry argument illustrated above) or no symmetry (by the arguments of Dewar, Olivella, and coworkers).[3,4] Consequently we undertook to characterize the electrocyclic reaction of $EO^{+\cdot}$ to find out whether the process could be described better by dispensing with the plane of symmetry imposed in the previous study,[5] and to add to our understanding of how symmetry constraints influence the course of chemical reactions. We also wanted to better characterize the electronic states of the ring-intact and the open forms of the ion.

RESULTS AND DISCUSSION

Electronic States of the Ring-intact Ion. Both MP2 and QCISD methods predict that the O ionized $^2B_1$ and C-C ionized $^2A'$ states of $EO^{+\cdot}$ exist in potential energy minima. Our calculation places the O ionized state 10.0 kJ/mol lower (Table 1). The methods agree that the $^2B_1$ has C_{2v} symmetry (Table 2) while the $^2A'$ state

Table 1

Energies of $C_2H_4O^{+\cdot}$ Species[a]

Ion	ZPVE[b]	E(QCISD)[c]	E[CCSD(T)][d]	ΔE(+2df)[e]	ΔE[b,f]
$^2B_1$	149.3	-1.022620	-1.064859	-0.082168	0.0
$^2A'$	154.4	-1.016272	-1.059744	-0.085432	10.0
$^2A_1$ TS	143.7	-1.009006	-1.052803	-0.085983	16.0
open form	140.8	-1.053424	-1.097188	-0.084589[g]	-99.7
disrot TS	142.7	-1.006060	-1.050267	-0.085392	23.2
conrot TS[h]	148.6	-1.002693	-1.047153	-0.086058	35.6
TS rotation about C-O in open form	145.6	-1.042924	-1.085352	-0.083480	-60.9

a. In hartrees unless otherwise noted. -152.000000 hartree should be added to all figures in hartrees. b. In kJ/mol. c. QCISD/6-311G*//QCISD/6-311G* d. CCSD(T)/6-311G**//QCISD/6-311G* e. PMP2/6-311+G(2df)//MP2/6-311G* - PMP2/6-311G*//MP2/6-311G* f. Relative to the $^2B_1$ state obtained by adding E[CCSD(T)], ΔE(+2df), and ZPVE. g. Equal C-O bond lengths (see text) h. At the MP2/6-311G* optimum geometry

has C_s symmetry about σ_v bisecting the C-C bond, that is, the hydrogens on each carbon have a disrotatory twist of about 16°. Figures 1 and 2 depict the O and C-C ionized forms respectively. Enforcing C_{2v} symmetry on the $^2A'$ state produces a TS between the two equivalent forms of the state with no tendency either to open up or to optimize to the $^2B_1$ state, although STABLE=OPT is necessary to avoid convergence of the SCF to the higher energy $^2B_1$ state in this geometry. This C_{2v} TS has C-O bonds (1.365 Å) 0.01 Å longer and a COC bond angle (80.9°) 5.5° larger than the stable C-C ionized form. A curiosity (for which we have no explanation) is that the O ionized state, which represents ionization from a nonbonding orbital. has a lower ZPVE than the C-C ionized state, which has had one bonding electron removed.

Table 2

Optimized Parameters of $C_2H_4O^{+\cdot}$ Ions[a]

	O Ionized	C-C Ionized	Disrot TS	Conrot TS[b]	Open Form[c]	TS Rotat about C-O
RC1O	1.483	1.375	1.307	1.347	1.3098	1.247
RC2O	1.483	1.375	1.409	1.350	1.3098	1.446
RC1H1	1.092	1.088	1.094	1.088	1.0887	1.094
RC1H2	1.092	1.092	1.093	1.087	1.0837	1.091
RC2H3	1.092	1.088	1.084	1.086	1.0887	1.085
RC2H4	1.092	1.092	1.087	1.088	1.0837	1.085
C2OC1	58.6	75.4	92.8	93.7	124.79	120.8
H1C1O	110.0	114.8	117.1	118.9	119.75	121.0
H2C1O	110.0	118.8	120.7	116.9	114.37	115.8
H3C2O	110.0	114.8	114.2	118.1	119.75	111.1
H4C2O	110.0	118.8	117.0	117.6	114.37	111.1
H1C1OC	-115.2	-117.8	-131.7	63.0	0.00	0.0
H2C1OC	115.2	85.8	54.6	-123.4	180.00	180.0
H3C2OC	115.2	117.8	102.0	73.6	0.00	-107.6
H4C2OC	-115.2	-85.8	-91.0	-112.1	180.00	107.6

a. Optimized at the QCISD/6-311G* level except for the conrotatory TS. The first six entries are bond lengths, entries 7-11 are bond angles, and entries 12-15 are dihedral angles. b. Optimized at the MP2/6-311G* level. c. Optimization with OPT=TIGHT

Asymmetry of the $^2A'$ state. It was puzzling why the C-C ionized form of $EO^{+\cdot}$ should have only C_s symmetry rather than the full C_{2v} symmetry of the neutral. A comparison of the orbital energies for this state in its

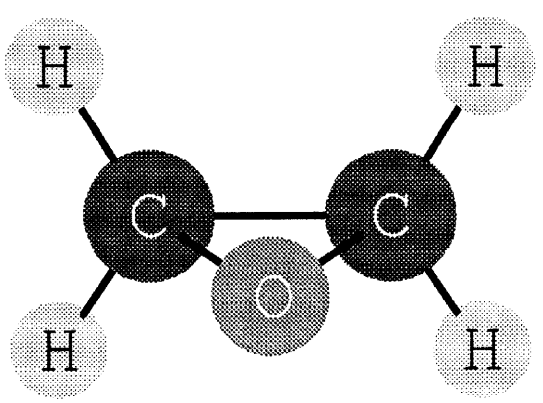

Figure 1

The Structure of the O Ionized Form

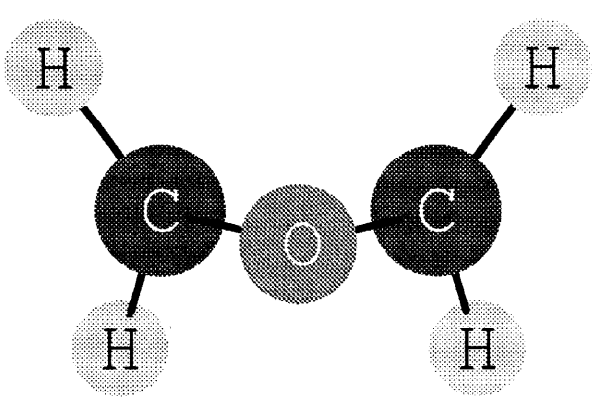

Figure 2

The Structure of the C-C Ionized Form

optimized form with those with the structure constrained to C_{2v} symmetry showed that the largest shifts occurred in the oxygen-centered orbitals ψ_1 (the oxygen 1s orbital) and ψ_{11} which is mostly devoted to the oxygen p_x orbital perpendicular to the ring in the C_{2v} constrained ion. The asymmetry is not an artifact of freezing the 1s MOs of the core. Optimizations without the frozen core restriction (MP2=FULL) did not change the finding that the lowest energy form of the ^2A state of $EO^{+\cdot}$ has lower symmetry than the neutral. The lowering of symmetry eliminates the distinction between a_1 and b_1 orbitals and between a_2 and b_2 orbitals, permitting them to mix. The b_1 orbital ψ_{11} mixes primarily with the a_1 SOMO ψ_{12}. This permits the p_z orbitals on oxygen in ψ_{11} to interact in a bonding way with the carbon orbitals in the center of the ring, and it also lessens the antibonding interaction between the p_x orbitals on oxygen and carbon. The introduction of oxygen and p_z components into ψ_{12} also lowers the energy of this MO, but less than it lowers the energy of ψ_{11}. The maximum amplitude of the oxygen orbitals in ψ_{12} is directed out of the plane of the heavy atoms and away from the rest of the molecule. The hydrogens in this ion lean away from the region of the molecule where the combination of oxygen orbitals in ψ_{12} has its maximum amplitude. The admixture of ψ_{11} and ψ_{12} of the C_{2v} form is revealed in the QCI density of the C_s form which shows a spin density of 0.361 on oxygen. Thus the designation "C-C ionized form", which is evident in the SCF density, is less clear in the QCI density. The neutral is not similarly asymmetric because it is more similar in geometry to the O ionized $^2B_1$ state, which has a different ordering of the energy levels.

The $^2A'$ state of the cyclopropyl radical must be much higher in energy relative to the $^2B_1$ state than it is in $EO^{+\cdot}$ because in the former it would involve a separation of charge that does not occur in the $^2A'$ state of $EO^{+\cdot}$. Consequently the electrocyclic reactions of the cyclopropyl radical and $EO^{+\cdot}$ are not necessarily governed by the same ideas, even though their ground states are isoelectronic.

Nature of the electrocyclic transition states. Conrotatory and disrotatory TSs exist for ring opening in MP2 theory. However, an attempt to optimize the MP2 conrotatory TS with QCISD theory produced the disrotatory TS in the 6-31G* basis set. In the 6-311G* basis set the MP2 conrotatory TS had the wrong curvature under QCISD optimization with two negative eigenvalues of the force constant matrix. The disrotatory TS exists and is highly unsymmetrical in both MP2 and QCISD (Table 2) theories. The conrotatory TS, which we were able to find only with MP2 methods, is also unsymmetrical, but less markedly so than the disrotatory TS. The QCISD/6-311G* optimized disrotatory TS and the MP2/6-311G* conrotatory TSs are depicted in figures 3 and 4 respectively.

For the disrotatory process the activation energy is 23.2 kJ/mol. We estimate that the conrotatory process has an activation energy of 35.6 kJ/mol. It is clear that the activation energy for ring opening is considerably less than the 110 kJ/mol predicted in the previous study.[5] We suggest that the higher energy of the conrotatory process, despite its formally allowed nature, is a result of the $^2A'$ state having a plane of symmetry, but not the requisite C_2 axis. Distortion of the C-C ionized $^2A'$ state into C_{2v} symmetry requires

6.0 kJ/mol according to our calculations. The difference in zero-point energies accounts for 5.9 kJ/mol of our predicted 12.4 kJ/mol difference between the conrotatory and disrotatory activation energies.

Nature of the reaction paths. IRC calculations show that the disrotatory reaction is highly asynchronous. The disrotatory TS has two nonequivalent methylenes. The one with the shorter bond to oxygen moves rapidly into planarity with the COC plane as the IRC calculations track the motions toward the open form. The plane of the other methylene remains nearly orthogonal to the COC plane. The hydrogens in this orthogonal methylene do not both begin to move in the disrotatory direction until the COC bond angle has opened up to at least 117°

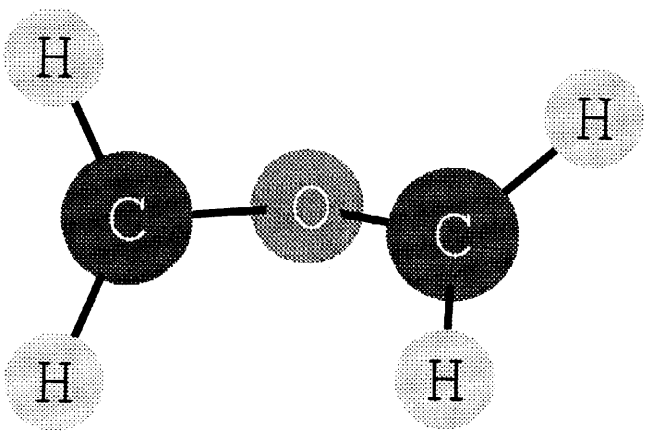

Figure 3
Structure of the Disrotatory TS

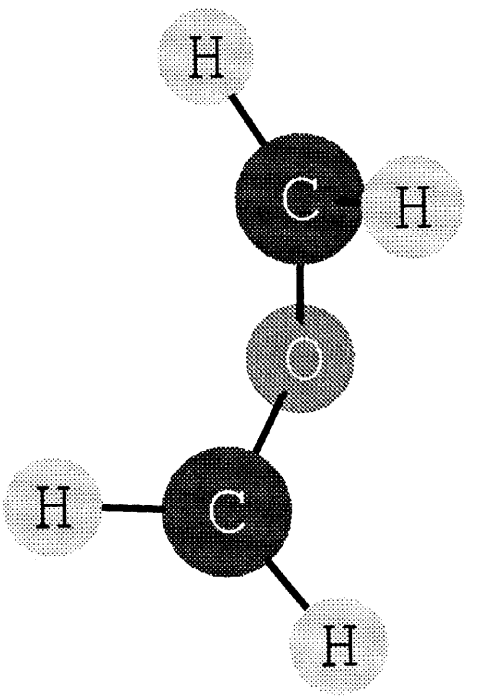

Figure 4
Structure of the Conrotatory TS

and the hydrogens on the other methylene are within 1.1° of planarity with the COC plane. Computations indicate that the cyclopropyl radical behaves very similarly.[4] In both cases the constraints of orbital symmetry against disrotatory ring opening are avoided by postponing the disrotatory motion of one methylene until the C-C σ bond is effectively broken and a C-O (C-C in the case of the cyclopropyl radical) π bond is nearly fully formed. Thus the apparent violation of the W-H rules in this disrotatory opening is really more of an evasion of the rules. We have found such evasions in 1,2 eliminations,[6] 1,3 sigmatropic shifts,[7] and in an electrocyclic reaction (this work). We suggest that such evasions are the usual course when there is no allowed path, no lower-energy fragmentation pathway, and the system is energized sufficiently.

In contrast, the conrotatory path is much more nearly synchronous. Although the two methylene groups

do not rotate at the same speed throughout the reaction, they do turn continuously in the same direction along the conrotatory path.

Open form of the ion. The ring-opened form of the ion is considerably more stable than either of the states with the ring intact. The open form lies 99.7 kJ/mol lower than the $^2B_1$ ground state by our calculations. Our results are in better agreement with the experimental results of 106.7 kJ/mol[8] than the previous computational study,[5] which placed the open form 58 kJ/mol below the O ionized form of the ring-intact ion.

QCISD methods predict that the open form of the ion is planar and has equal C-O bond lengths, although this is only evident in the 6-311G* basis set with the 30 fold reduction in convergence criteria one gets with OPT=TIGHT. Both results are in conflict with those of the previous study[5]. The open form of the ion is depicted in Fig. 5. MP2 theory (and UHF theory in the 6-311G* basis set) concur on the planarity of

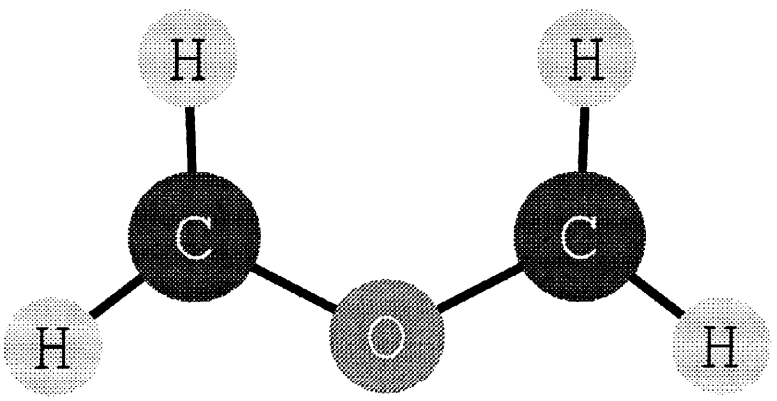

Figure 5

Structure of the Open Form

the ring-opened ion. We find the TS for rotation of one of the CH_2 groups 38.8 kJ/mol above the planar form. It was hard to understand why the ion should not be conjugated as in the earlier study[5] which found the H_2CO plane containing the longer C-O bond to be at right angles to the H_2COC plane containing the shorter C-O bond.

Our MP2 results predict unequal C-O bond lengths. However, when the zero-point energies are added, the TS for interchange of the long and short C-O bonds is lower in energy than the optimized structure. The PMP2 energy of the open form of the ion with equal C-O bond lengths is lower than the PMP2 energy of the species with UMP2 optimized parameters. Therefore we conclude that the C-O bond lengths are equal, and

that the open form has C_{2v} symmetry.

The UHF wave function of the open form of the ion has $<s^2>$ of about 0.9. Consequently we consider the PMP2 energy to form a more valid basis for comparison of energies when the open form is involved in the comparison. Our QCISD runs provide direct evidence of this (Table 3). More than 97 per cent of the total change in energy of the open ion as higher multiplicities are removed by projection occurs upon annihilation

Table 3

Projected MP2 Energies[a]

Multiplicities of states removed by projection	Energies	
	Open Ion	C-C Ionized
none (UMP2)	-153.015053	-152.983938
4	-153.028127	-152.986290
4, 6	-153.027771	-152.986272
4, 6, 8	-153.027772	-152.986272
4, 6, 8, 10	-153.027772	-152.986272

a. At the QCISD/6-311G* optimum geometry, in the 6-311G* basis set.

of the quartet contaminant. Table 3 also contains the data for the C-C ionized form of the ion for comparison. Annihilation of the quartet state changes the energy of the open form 5.6 times as much as it changes the energy of the C-C ionized form. We conclude that spin projection is important for an adequate description of the open ion.

FACILITIES AND METHODS

The computations were performed on a Cobra Carrera computer containing a DEC Alpha processor utilizing the GAUSSIAN 94[9] suite of programs. Our MP2 and QCISD calculations are with frozen core. All

stationary points were shown to have the correct number of real vibrational frequencies by calculating them at the MP2/6-31G* level on tightly optimized structures. Force constants for QCISD transition states were calculated at the MP2/6-311G* level. The MP2/6-31G* zero point energies are unscaled. Since the gross structure of the open ion as optimized by MP2 methods differs from that calculated by QCISD methods, the vibrational frequencies and zero-point energy for this species computed at the MP2 level may be of lesser accuracy than the others. However, it is very unlikely that the inaccuracy in the zero point energy for this species would affect the order of the stationary points we calculated. We used CCSD(T) not only to estimate the effect of triple substitutions, but also to check on the consistency of the ordering of our stationary points between high levels [QCISD and CCSD(T)] of computation. Since the order of the states is the same with these two methods, we believe that our order is correct. (MP2 methods place the C-C ionized state comparable to, or lower than the O ionized state.) We estimated the effect of diffuse functions, a second set of d orbitals, and f orbitals on the heavy atoms at the MP2 level. The only species encountered in this study that did not have a UHF wave function with $\langle s^2 \rangle$ between 0.75 and 0.8 was the ring opened ion. To facilitate comparisons to this ion whose $\langle s^2 \rangle$ is about 0.9, MP2 energies computed in the $\Delta E(+2df)$ correction are the PMP2 energies of UMP2 optimized structures with the exception of the open form. The $\Delta E(+2df)$ correction for the open ion was for the structure optimized with constraint to equal C-O bond lengths, since that seems to be the correct structure of the ion. The ring-opening TSs were confirmed as disrotatory and conrotatory by IRC calculations at the MP2/6-31G* level. At the MP2 level the search for the electrocyclic TSs by simply fixing the COC bond angle and optimizing the other parameters led to separate potential energy surfaces (PESs) depending upon whether the TS was approached from the open form of the ion or the C-C ionized state. Consequently an exploration of the region between these PESs was necessary. Fortunately, a simple average of the optimized parameters landed on a point of the correct curvature, and the TS finding routine converged to the proper disrotatory TS. The same problem was encountered in searching for the conrotatory TS. However, the points we tried had two negative eigenvalues of the force constant matrix. We then attempted to find a second order saddle point for this process. This run was aborted when the routine stepped into a region with only one negative eigenvalue of the force constant matrix. From this point the TS finding routine located the conrotatory

TS at the MP2 level. We could not locate the conrotatory TS using QCISD methods.

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