An ab Initio Molecular Orbital Study of the Structures and Stabilities of the $C_2H_4O^{+\cdot}$ Isomers

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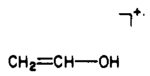
Abstract: A detailed study of 11 possible $C_2H_4O^{+\cdot}$ isomers has been carried out with the aid of ab initio molecular orbital theory. Calculations have been performed with minimal (STO-3G), split-valence (4-31G), and split-valence + polarization (6-31G*) basis sets and with restricted (RHF) and unrestricted (UHF) Hartree-Fock procedures. Geometries have been fully optimized and relative energies calculated. Three well-established $C_2H_4O^{+\cdot}$ isomers ($CH_2{=}CHOH^{+\cdot}$, $CH_3CHO^{+\cdot}$, and $\overline{CH_2OCH_2}{}^{+\cdot}$) and a fourth more recently postulated isomer ($CH_2OCH_2^{+\cdot}$) are all found to be stable structures and to have relatively low energies. Five additional isomers ($CH_2CH_2O^{+}$, $CH_3C{=}OH^{+\cdot}$, $CH_3O{=}CH^{+\cdot}$, $CH{=}CHOH_2^{+\cdot}$, and $CH_2{=}COH_2^{+\cdot}$) have been identified as having reasonable prospects for experimental observation. The reaction paths for the possible interconversion of the closed ethylene oxide ion to the two ring-opened isomers have been examined.

Introduction

There has been considerable recent interest in the study of the structures and stabilities of isomeric gas-phase cations. In this respect the $C_2H_4O^{+\cdot}$ isomers have been studied using a variety of experimental techniques. McLafferty, using collisional activation,[1] distinguished three noninterconvertible species corresponding to the molecular ions of vinyl alcohol (**1**), acetaldehyde (**2**), and ethylene oxide (**3**). Thermochemical measurements by Holmes et al.[2] provided the heats of formation for these three isomers. In a metastable ion study, Holmes and Terlouw[3] also observed transitions corresponding to decompositions of these three isomers and, in addition, suggested that the *m/z* 44 ion from ethylene glycol dimethyl ether might be a fourth isomer. Blair and Harrison,[4] as a result of studying ion-molecule reactions using an ion trapping technique, reported reactions of an "activated" ethylene oxide ion derived from the ethylene oxide molecular ion. ICR investigations by Beauchamp[5] of the reactions of the ethylene oxide ion led to the proposal that the reacting species which transfers $CH_2^{+\cdot}$ to neutral ethylene oxide is a C···C ring-opened form (**4**). Kumakura,[6] however, also studied the reactions of this *m/z* 44 ion, and postulated the alternative C···O ring-opened species **5**. Recently, we reported[7] an ICR study in which we provided evidence in support of structure **4** rather than **5** as the reacting $C_2H_4O^{+\cdot}$ isomer produced from ethylene oxide and from 1,3-dioxolane.

The identification of the structures of the different isomers of gas-phase cations is important since knowledge of the structures of these ions can assist in understanding mass spectrometric rearrangement and fragmentation processes. In combination with our ICR study[7] of the $C_2H_4O^{+\cdot}$ isomers, we have undertaken an ab initio molecular orbital study of these isomers in which we have examined 11 potentially stable species (**1–11**).


$CH_2{=}CH{-}OH\rceil^{+\cdot}$

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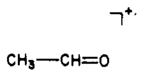
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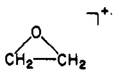

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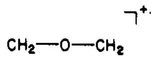
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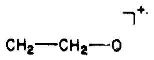
$CH_2{-}CH_2{-}O\rceil^{+\cdot}$

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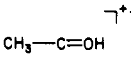
$CH_3{-}C{=}OH\rceil^{+\cdot}$

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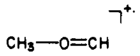
$CH_3{-}O{=}CH\rceil^{+\cdot}$

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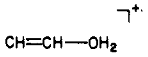
$CH{=}CH{-}OH_2\rceil^{+\cdot}$

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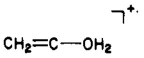
$CH_2{=}C{-}OH_2\rceil^{+\cdot}$

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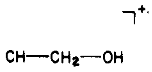
$CH{-}CH_2{-}OH\rceil^{+\cdot}$

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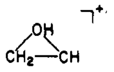

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In undertaking this study, we had three principal objectives, namely, to determine (1) those isomers which are at minima in the $C_2H_4O^{+\cdot}$ potential energy surface, and thus might occur as stable ionic species, (2) the structures of these isomers, and (3) the relative energies of these isomers. This work supplements concurrent studies of the $CH_2O^{+\cdot}$ [8] and $C_3H_6O^{+\cdot}$ [9] systems.

Methods and Results

Standard LCAO-SCF-MO calculations were carried out using a modified version of the GAUSSIAN 70 system of programs,[10,11] employing the restricted[12] and unrestricted[13] Hartree-Fock procedures and the STO-3G,[14] 4-31G,[15] and 6-31G* [16,17] basis sets. The last basis set is most reliable for energy predictions. Our initial study concerned the isomers of special interest **1–5**. The geometries of all isomers were optimized, subject only to specified symmetry constraints (C_{2v} for **3**, C_1 for **11**, C_s for the remaining isomers) using the RHF procedure, at the STO-3G level, followed by single energy calculations at the 4-31G and 6-31G* levels (denoted RHF/4-31G//RHF/STO-3G and RHF/6-31G*//RHF/STO-3G). For comparison, we repeated this study employing the UHF procedure, yielding UHF/STO-3G geometries and UHF/4-31G//UHF/STO-3G energies. Finally, we optimized **1–5** at the RHF/4-31G level.[18] Similar geometries were obtained using these various approaches.

To examine the possible ring opening of the ethylene oxide ion (**3**), we studied the reaction profiles for C–C and C–O bond fission, using the UHF/4-31G//UHF/STO-3G approach. C–C bond fission will lead to the C···C ring-opened form **4**, and a suitable reaction coordinate is the COC angle. C–O bond fission can give rise to the C···O ring-opened ion **5**; here the CCO angle is a suitable reaction coordinate. The results are presented in Figures 1 and 2.

The remaining isomers **6–11** were studied by optimizing geometries at the RHF/STO-3G level alone in the belief that the RHF/6-31G*//RHF/STO-3G energies are likely to be sufficiently reliable for our purposes. The calculated total and relative energies are listed in Table I. Parts of the potential energy surface interconnecting some of the additional $C_2H_4O^{+\cdot}$ isomers were also examined (at the RHF/4-31G//RHF/STO-3G level) and are discussed below.

Optimized structures for all the ions studied are displayed

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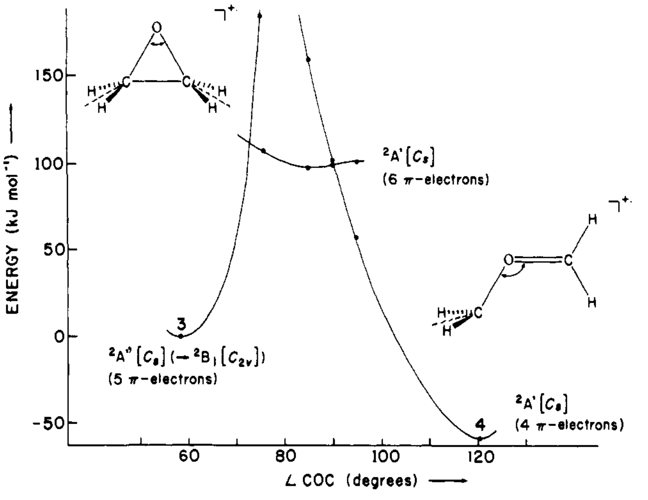


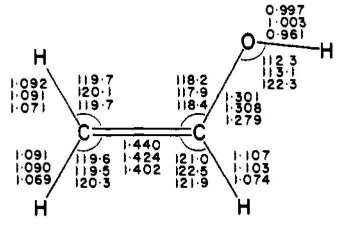
Figure 1. Reaction profile (UHF/4-31G//UHF/STO-3G) for the ring opening of the closed ethylene oxide ion (3) by C-C bond fission. The number of π electrons for the systems described by the individual potential curves is shown in brackets.

within the Discussion section. Unless otherwise noted, these refer to RHF/STO-3G results. For ions **1-5** where optimizations were also carried out at the UHF/STO-3G and RHF/4-31G levels, all three sets of parameters are shown in the order RHF/STO-3G, UHF/STO-3G, and RHF/4-31G. Throughout this paper, bond lengths are in ångstroms and bond angles in degrees.

Discussion

Comparative Study of Isomers 1-5. Since experimental techniques had established the existence of **1**, **2**, and **3** as stable, noninterconverting isomers of $C_2H_4O^{+\cdot}$, and **4** and **5** had been postulated as possible fourth and fifth isomers, we carried out an initial study of these species. All five isomers were optimized at the RHF/STO-3G, UHF/STO-3G, and RHF/4-31G levels. Though producing lower energies than RHF, the UHF procedure is known to occasionally run into problems due to contamination from states of higher spin multiplicity.[19] The present study provides a further comparison between the two procedures.

$CH_2{=}CHOH^{+\cdot}$ (1). In agreement with thermochemical measurements,[2] the vinyl alcohol radical cation is found to be the lowest energy $C_2H_4O^{+\cdot}$ isomer. Noteworthy is the position of the hydroxyl hydrogen, which is found to be anti in the radical cation, whereas in neutral vinyl alcohol it is found to be syn, both experimentally[20] and theoretically.[21] For the radical cation, the syn isomer is found to be 12.7 kJ mol^{-1} (with RHF/4-31G//RHF/STO-3G as well as UHF/4-31G//UHF/STO-3G) higher than the anti isomer.[22] When we examine the highest occupied molecular orbital (HOMO) in the neutral, and the singly occupied molecular orbital (SOMO) in the radical cation, we find that the electron has been removed from a π orbital (**12**). Removal of an electron from this orbital would be expected to, and indeed does, lead to a lengthening of the C=C bond (+0.13 Å with RHF/STO-3G,[23] +0.11 Å with UHF/STO-3G, and +0.09 Å with RHF/4-31G[24]) and a shortening of the C—O bond (e.g., −0.09 Å with RHF/4-31G).



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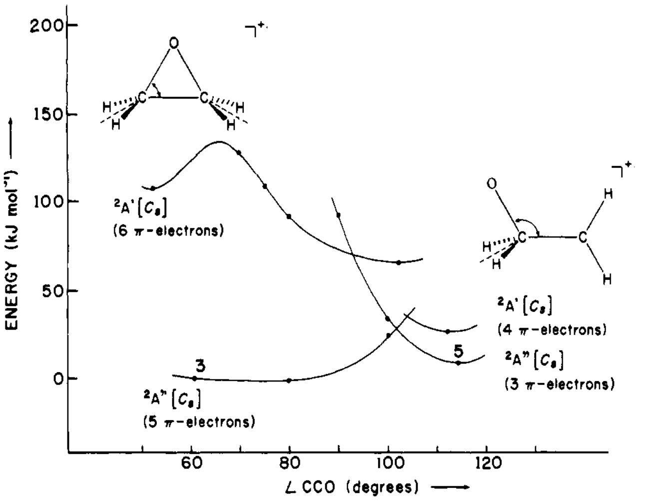
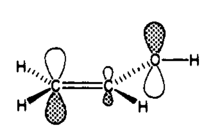


Figure 2. Reaction profile (UHF/4-31G//UHF/STO-3G) for the ring opening of the closed ethylene oxide ion (3) by C-O bond fission. The number of π electrons for the systems described by the individual potential curves is shown in brackets.



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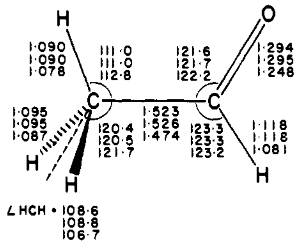
$CH_3CH{=}O^{+\cdot}$ (2). The relative energy of **2** with respect to **1** is found to be 52.3 kJ mol^{-1} at the RHF/6-31G*//RHF/STO-3G level, which is slightly larger than the values at the RHF/4-31G and UHF/4-31G levels but in reasonable agreement with the experimentally[2] determined value of 63 kJ mol^{-1}. Our calculations show that, as found for the neutral acetaldehyde, the radical cation has one C—H bond eclipsing the C=O bond. The rotational barrier is found to be 3.3 kJ mol^{-1} (with RHF/4-31G//RHF/STO-3G as well as UHF/4-31G//UHF/STO-3G[25]), which is close to the barrier calculated (3.1 kJ mol^{-1}) for the neutral system.[26] Examining the HOMO for neutral acetaldehyde and the SOMO for the radical cation, we find that the orbital in each case is a σ orbital, with the largest coefficient on the oxygen (**13**). This implies that the odd electron resides mainly on the oxygen. Comparing the optimized geometries for the neutral[23,24] and the ion, we find a slight shortening of the C—C bond



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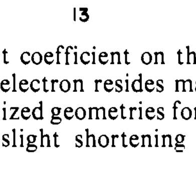

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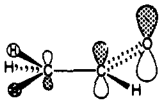
Table I. Calculated Total Energies (hartrees) and Relative Energies (kJ mol^{-1}) for the $C_2H_4O^{+\cdot}$ Isomers

			RHF/STO-3G[a]		RHF/4-31G//RHF/STO-3G[a]		RHF/6-31G*//RHF/STO-3G[a]	
isomer	symmetry	state	total	rel	total	rel	total	rel
1	C_s	$^2A''$	−150.689 63	0	−152.371 39	0	−152.599 96	0
2	C_s	$^2A'$	−150.709 59	−52.4	−152.355 45	41.9	−152.580 05	52.3
3	C_{2v}	$^2B_1$	−150.682 91	17.6	−152.297 80	193.2	−152.530 41	182.6
4	C_s	$^2A'$	−150.660 22	77.2	−152.321 24	131.7	−152.552 38	124.9
5	C_s	$^2A''$	−150.632 40	150.3	−152.295 83	198.4	−152.509 58	237.3
6	C_s	$^2A'$	−150.682 32	19.1	−152.343 67	72.8	−152.572 44	72.3
7	C_s	$^2A'$	−150.661 69	73.4	−152.317 30	142.0	−152.547 88	136.7
8	C_s	$^2A'$	−150.630 08	156.3	−152.311 61	157.0	−152.518 91	212.8
9	C_s	$^2A'$	−150.626 94	164.6	−152.304 08	176.7	−152.511 14	233.2
10	C_s	$^2A'$	−150.578 23	292.5	−152.258 79	295.6	−152.481 31	311.5
11	C_1	^2A	−150.643 18	122.0	−152.280 58	238.4	−152.516 34	219.5

	UHF/STO-3G[a]		UHF/4-31G//UHF/STO-3G[a]		RHF/4-31G[a]	
isomer	total	rel	total	rel	total	rel
1	−150.696 95	0	−152.375 21	0	−152.378 06	0
2	−150.714 38	−45.8	−152.359 50	41.2	−152.360 40	46.4
3	−150.685 66	29.6	−152.301 09	194.6	−152.303 89	194.7
4	−150.662 50	90.4	−152.323 44	135.9	−152.327 24	133.4
5	−150.633 54	166.5	−152.297 61	203.7	−152.302 21	199.1

[a] See text for description of notation.

(e.g., −0.02 Å with RHF/4-31G) and a lengthening of the C═O bond (e.g., +0.04 Å with RHF/4-31G). This suggests that the observed structural changes may involve the highest occupied π orbital even though it is not the SOMO. When we examine this orbital for the neutral (**14**) and the ion (**15**) we see that the change in this orbital is consistent with the observed structural change upon ionization: the antibonding character in the C—C bond has decreased, and also the bonding character in the C═O bond has decreased.



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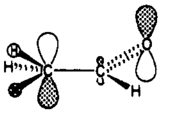

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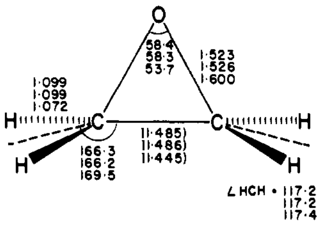
$CH_2OCH_2^{+\cdot}$ (**3**). Our best estimate for the relative energy of the ethylene oxide cation **3** is 182.6 kJ mol^{-1} (RHF/6-31G*//RHF/STO-3G), which is slightly lower than the 4-31G results (Table I) but quite close to the experimental value[2] of 209 kJ mol^{-1}. The HOMO and SOMO of ethylene oxide and its radical cation have π symmetry and are almost exclusively located on the oxygen (**16**). This is in agreement with photoelectron studies[27] which show that **3** is formed by removal of an electron from the $2b_1$ π-type orbital which is largely localized on the oxygen atom. Comparison of the optimized geometries of neutral ethylene oxide[24] and its radical cation, however, shows a lengthening of the C–O bonds (e.g., +0.14 Å with RHF/4-31G) upon ionization. A rationalization of this increase can be found by looking at the highest doubly occupied π-type orbital (not the HOMO) for the neutral (**17**) and the ionic (**18**) species. Whereas in **17** the molecular orbital is providing bonding between all three heavy atoms, the molecular orbital in **18** is centered mainly on the carbon atoms, which may account for the observed shortening of the C–C and lengthening of the C–O bonds.



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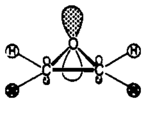

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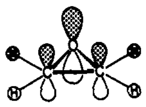

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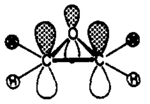

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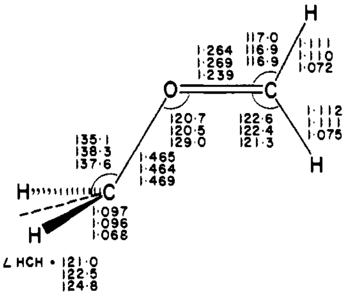

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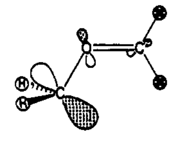
$CH_2OCH_2^{+\cdot}$ (**4**). This ion, which can be considered to arise from the ethylene oxide radical cation by cleavage of the C–C bond, is a particularly interesting species. In agreement with the proposal of Beauchamp,[5] our ICR experiments[7] have substantiated the existence of a C···C ring-opened isomer of $C_2H_4O^{+\cdot}$. Our work showed that this isomer can be generated from 1,3-dioxolane, which has a prominent fragment ion at m/z 44. In a collisional activation study of the $C_2H_4O^{+\cdot}$ isomers McLafferty reported[1] that this m/z 44 ion from 1,3-dioxolane was a mixture of **1** and **3**. However, Holmes et al. determined the heat of formation of this ion, and found it to be about 109 kJ mol^{-1} lower in energy than **3** yet higher than that of **1** by 100 kJ mol^{-1}. Our calculations show that C···C ring-opened ethylene oxide isomer (**4**) to be some 58 kJ mol^{-1} lower in energy than **3**. On the basis of theoretical[18] and experimental[5,7] results we consider that, in addition to the three well-established isomers of $C_2H_4O^{+\cdot}$ (**1–3**), there is persuasive evidence for the existence of **4** as a fourth stable isomer. The calculated geometry of **4** has some interesting features. One C–O bond is much shorter than the other, and the CH_2 group on the side with the weaker C–O bond is perpendicular to the plane of the rest of the molecule. This suggests a significant contribution of the asymmetric valence structure **19b**. This geometry pro-

$$\dot{C}H_2\text{—O—}\dot{C}H_2 \longleftrightarrow \dot{C}H_2\text{—}\dot{O}\text{=}CH_2$$

19a **19b**

vides an immediate rationalization for the observed ion–molecule reactions[4,5,7] of **4** in which it transfers a $CH_2^{+\cdot}$ moiety to the neutral molecule with which it reacts. The SOMO (**20**)



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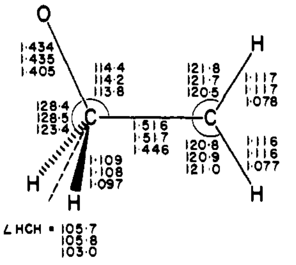
of **4** demonstrates the radical character at the carbon of the perpendicular CH_2 group.

$CH_2CH_2O^{+\cdot}$ (5). In contrast to the proposal by Kumakura et al.,[6] there is to date no experimental ICR evidence to support the existence of a stable $C_2H_4O^{+\cdot}$ isomer corresponding to the $CH_2CH_2O^{+\cdot}$ structure.[7] Initial optimizations of structure **21** at both RHF/STO-3G and UHF/STO-3G levels led directly to structure **3**, i.e., the closed ethylene oxide radical cation. However, rotation of the terminal methylene group in **21** did lead to a stable structure **5**. This rotational preference can be rationalized by hyperconjugative interaction. The oxygen is strongly σ-electron withdrawing, and has therefore a relative destabilizing interaction with the neighboring cationic center (**21a**). Thus we find **5** to be the preferred conformation, a result similar to that obtained[28] for $FCH_2CH_2^+$. The energy of **5** relative to **3** is 54.7 kJ mol^{-1} (RHF/6-31G*//RHF/STO-3G). In this case, the relative energy is substantially larger with 6-31G* than 4-31G.



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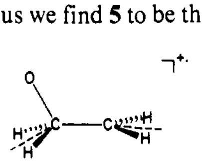

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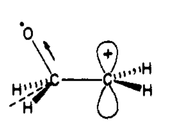


21a

Comparisons of Theoretical Procedures. Having studied these five $C_2H_4O^{+\cdot}$ isomers in detail, we are able to compare the RHF/6-31G*//RHF/STO-3G results with the RHF/4-31G//RHF/STO-3G, UHF/4-31G//STO-3G, and RHF/4-31G results. The relative energies calculated with all four methods are generally very similar, with only isomer **5** showing a substantial difference between the more reliable 6-31G* results and those of the simpler calculations. The RHF/4-31G/RHF/STO-3G results are very similar to those with RHF/4-31G, indicating that, for these systems at least, there is no significant advantage in optimizing at the 4-31G level. As far as the optimized geometries are concerned, differences between STO-3G and 4-31G results are similar to those reported previously.[29] It is noteworthy, however, that STO-3G and 4-31G predict similar *changes* in geometry when going from the neutral species to the corresponding ions. Finally, we note the generally good agreement between the RHF and UHF structures for the $C_2H_4O^{+\cdot}$ isomers **1–5**. Even for multiple bonds, for which the differences between UHF and RHF have been previously found to be large because of contamination of UHF by states of higher multiplicity,[19] the results obtained by the two methods are very similar. The largest difference found in our study is for the C=C bond of **1** (0.016 Å); for the other bonds between heavy atoms we find differences smaller than 0.007 Å. Very small differences are also found for C–H bond lengths and CCH and OCH bond angles.

Ring Opening in the Ethylene Oxide Radical Cation. In order to assess the stability of the closed ethylene oxide ion **3** with respect to ring opening to give the open ethylene oxide ions **4** or **5**, we have examined the potential energy surfaces linking **3** with **4** and **3** with **5** using the 4-31G//STO-3G approach. For the study of the ring opening, we have employed the UHF method, in the expectation that this method should provide a better description of intermediate regions on the $C_2H_4O^{+\cdot}$ potential energy surface.

Fission of the Carbon–Carbon Bond. We have chosen the COC angle as a convenient reaction coordinate. For fixed values of ∠COC, we have fully optimized a number of structures subject only to a C_s symmetry constraint. For the closed ethylene oxide ion (**3**), we find that the best C_s structure actually has C_{2v} symmetry leading to a ground state of $^2A''(C_s) \rightarrow {}^2B_1(C_{2v})$. In this structure we have five electrons in π-type orbitals, as indicated in Figure 1. As the COC angle widens from its value in **3**, the optimized structures continue to have C_{2v} symmetry, and the energy rises rapidly. When ∠COC is larger than 72° the $^2A'(C_s)$ state (with six π electrons) becomes energetically more favorable. For ∠COC between 72 and 90°, these structures prefer C_{2v} symmetry over C_s symmetry. This state has a potential energy minimum at ∠COC = 75.6° (UHF/STO-3G), which at the 4-31G/STO-3G level has shifted somewhat toward a larger COC angle. At ∠COC = 90° this $^2A'$ state becomes isoenergetic with a second $^2A'(C_s)$ state with four π electrons. The latter leads to the open ethylene oxide ion **4**, which has a stable minimum for ∠COC = 120.5°. Going from the $^2A'$ (six π electron) state to the $^2A'$ (four π electron) state requires rotation of one of the CH_2 groups by 90°, leading to coplanarity of this group with the heavy-atom system. This rotation is likely to take place when ∠COC ~ 90°. Optimization of an ion with ∠COC = 90°, and one CH_2 group rotated through 45°, showed only a slight increase in energy (~4 kJ mol^{-1}) over the unrotated form.

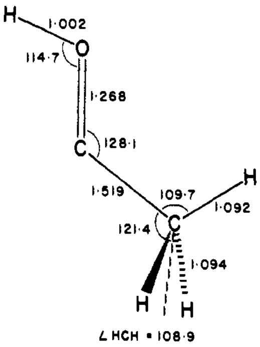
Thus we find that interconversion of **3** to **4** initially requires a crossing of electronic states from $^2B_1$ to $^2A'(\rightarrow {}^2A_1)$, with a barrier of approximately 110 kJ mol^{-1}. This transition from $^2B_1$ to $^2A_1$ is possible through coupling of the $^2B_1$ electronic state with vibrations of b_1 symmetry[30] (CH_2 asymmetric stretch, CH_2 twist, and CH_2 rock). The subsequent conversion from the $^2A'$ (six π electron) state to the $^2A'$ (four π electron) state requires little energy, indicating that the barrier to ring opening of **3** to give **4** is likely to be ~110 kJ mol^{-1}.

Fission of the Carbon–Oxygen Bond. For this ring opening, the CCO angle was chosen as reaction coordinate. Our UHF/4-31G calculations predict that the ground state of the closed ethylene oxide ion **3** ($^2A''(C_s) \rightarrow {}^2B_1(C_{2v})$, five π electrons) allows for extensive deformation of **3** with little change in energy (see Figure 2). The excited state of **3** ($^2A'(C_s)$, six π electrons) lies higher in energy. The C···O ring-opened form of the ethylene oxide ion **5** has a $^2A''$ (three π

electron) ground state with a $^2A'$ (four π electron) state lying several kJ mol^{-1} higher in energy. Rearrangement of **5** to **3** can take place by rotation of the terminal methylene group through 90° coupled with ring closure. At the UHF/4-31G//UHF/STO-3G level, the barrier is 25–30 kJ mol^{-1} and occurs at $\angle$CCO $\sim$ 102°. At the 6-31G* level, the relative energy of **5** is increased and the barrier to rearrangement to **3** is likely to be decreased.

Stability of the Ethylene Oxide Radical Cation. This study of the two possible modes of ring opening indicates that the C–O bonds in **3** are relatively weak, and can easily be broken; i.e., the ring-closed ethylene oxide ion **3** and its C···O ring-opened isomer **5** are separated by only a small energy barrier. Fission of the C–C bond requires more energy. Thus the barrier to ring opening of **3** to give its C···C ring-opened isomer **4** is approximately 105–120 kJ mol^{-1}. However, **4** when formed should be quite stable since it lies about 58 kJ mol$^-$ lower in energy than **3**.

RHF Study of Isomers 6–11. $CH_3C{=}OH^{+\cdot}$ (6). This isomer has a surprisingly low energy of 72 kJ mol^{-1} relative to **1**. The occurrence of **6** as an unstable intermediate formed by CO$_2$ loss from the pyruvic acid molecular ion had been previously postulated by Turro et al.,[31] where they assumed subsequent isomerization of **6** to the acetaldehyde radical cation (**2**). In their metastable ion study, Holmes and Terlouw[3] also studied the *m/z* 44 ion from the pyruvic acid molecular ion, and found it to correspond to **1** rather than **2**. They did note the possibility of an unknown $C_2H_4O^{+\cdot}$ isomer occurring as well. We have investigated the two possible isomerizations of **6** by way of 1,2-hydrogen shifts to **1** and **2** by optimizing structures in which the moving hydrogen is halfway along the C–C or C–O bond (**22, 23**). This leads to lower limits for the barriers of 167 and 264 kJ mol^{-1}, respectively (RHF/4-31G//RHF/STO-3G). We note that the results of more sophisticated calculations suggest a barrier of ~180 kJ mol^{-1} for the rearrangement analogous to **6** → **2** in the $CH_2O^{+\cdot}$ system.[8] These results support the experimental findings of Holmes and Terlouw (namely, that **6** is more likely to rearrange to **1** than **2**), but also suggest that under the appropriate conditions **6** might be sufficiently stable to be experimentally identified.



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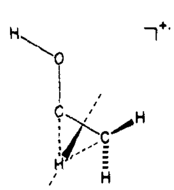

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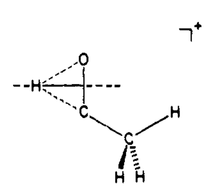
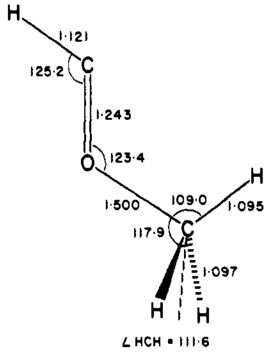


23

$CH_3O{=}CH^{+\cdot}$ (7). This isomer, like the one previously discussed, can be considered to correspond to the molecular ion of a carbenoid species, in this case methoxymethylene. The energy calculated relative to **1** is 137 kJ mol^{-1}, which is lower than that of one of the observed isomers **3**. Although it has not yet been detected experimentally, there seems to be a reasonable prospect of **7** occurring as a stable $C_2H_4O^{+\cdot}$ isomer if a suitable precursor ion species can be found.



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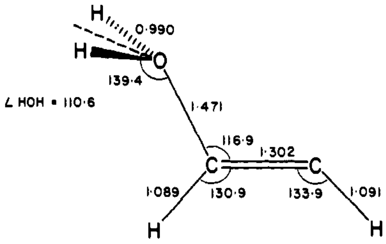
$CH{=}CHOH_2^{+\cdot}$ (8). This isomer, which is somewhat higher in energy, was also found to lie at a potential minimum in the $C_2H_4O^{+\cdot}$ surface. The short C—C bond and the long C—O bond suggest that it might be considered a complex of H$_2$O and $HC{\equiv}CH^{+\cdot}$. At the RHF/4-31G//RHF/STO-3G level, this complex is calculated to be 162 kJ mol^{-1} more stable than separated H$_2$O and $HC{\equiv}CH^{+\cdot}$.[32] By selecting the C–O bond length as reaction coordinate, we find that dissociation of the complex passes through a structure with C_{2v} symmetry. The optimized C_{2v} structure (**24**) can be considered to be the transition state for the degenerate isomerization of **8**. This isomerization is similar to that previously studied[34] for the complex of H$_2$O and $H_2C{=}CH_2^{+\cdot}$. The barrier calculated for the isomerization of **8** (73 kJ mol^{-1} at RHF/4-31G/RHF/STO-3G) is somewhat higher than the barrier found for $CH_2CH_2OH_2^{+\cdot}$ (35 kJ mol^{-1} with UHF/4-31G//UHF/STO-3G). Attempts to generate **8** via reaction of ionized acetylene and water (or vice versa) have proved unsuccessful.[35]



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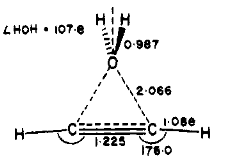

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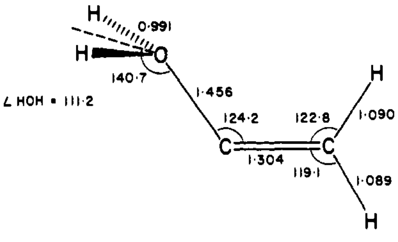
$CH_2{=}COH_2^{+\cdot}$ (9). This isomer can, by analogy with **8**, be considered as a complex of vinylidene radical cation and water.



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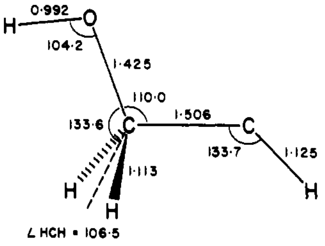
It is only slightly higher (20 kJ mol^{-1}) in energy than **8**. However, we note that an isomerization by means of a 1,2-hydrogen shift could lead to the most stable $C_2H_4O^{+\cdot}$ isomer, **1**. Considering that **9** is 233 kJ mol^{-1} higher in energy than **1**, the barrier for this isomerization might be small.

$\mathrm{CHCH_2OH^{+\cdot}}$ (10). Included in our study is another possible isomer is **10**. The structure is found to prefer C_s symmetry with distortions leading to an increase in energy. **10** is found to be extremely high in energy, and is thus unlikely to be significant experimentally.



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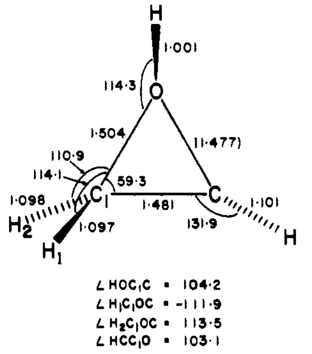
$\overline{\mathrm{CHCH_2O}}\mathrm{H^{+\cdot}}$ (11). Structure **11** is a ring-closed isomer of **10** and is also of quite high energy. Although **11** is significantly lower in energy than **10**, we do not find the ring closure to occur without a barrier.



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Conclusions

The main points arising from this study are as follows.

(1) Consistent with experimental studies, our calculations indicate that the experimentally observed $C_2H_4O^{+\cdot}$ isomers, namely, the vinyl alcohol (**1**), acetaldehyde (**2**), ethylene oxide (**3**), and open ethylene oxide (**4**) radical cations, are relatively low energy species which are stable with respect to intramolecular rearrangement. The calculated relative energies for **1**, **2**, and **3** are in reasonable agreement with thermochemical data.

(2) The C···O ring-opened ethylene oxide cation (**5**) has an energy higher than that of the ring-closed form (**3**).

(3) Fission of the C-C bond in the closed ethylene oxide ion (**3**) to produce the more stable C···C ring-opened isomer (**4**) requires about 105-120 kJ mol^{-1}.

(4) Four other isomers (**6-9**) of $C_2H_4O^{+\cdot}$ have been identified as having reasonable prospects for experimental observation. ICR studies to probe for their existence are in progress.

(5) From our comparison of theoretical procedures for studying isomers **1-5**, we note two important points: (a) For the radical cations studied here, the RHF and UHF methods give comparable results. (b) The relative energies obtained from RHF/4-31G single point calculations at RHF/STO-3G optimized structures are very similar to those obtained from full RHF/4-31G optimizations. This demonstrates the usefulness of the RHF/4-31G//RHF/STO-3G approach.

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(25) Optimized structural parameters [RHF/STO-3G(UHF/STO-3G)] for the staggered acetaldehyde radical cation follow: C—C 1.528 (1.520), C═O 1.295 (1.295), C—H_t 1.088 (1.089), C—H_s 1.095 (1.094), C—H 1.119 (1.118) Å; ∠CCO 121.4 (121.4), ∠H_tCC 109.1 (108.8), ∠CCH_{ss} 122.8 (123.2), ∠HCC 124.0 (124.1), ∠H_sCH_s 109.0 (109.2)°. H_t denotes the methyl hydrogen trans with respect to O, H_s denotes the methyl hydrogens staggered with respect to O, and H_{ss} denotes the H_sCH_s plane. Total energies follow: RHF/STO-3G, −150.707 97; RHF/4-31G//RHF/STO-3G, 152.354 18; UHF/STO-3G, −150.712 85; UHF/4-31G//UHF/STO-3G, −152.358 24 hartrees.
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