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# Structures and Stabilities of Gas-Phase $C_2H_3O^+$ Ions: An ab Initio Molecular Orbital Study

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**Abstract:** Ab initio molecular orbital theory has been used to examine the structures and stabilities of gas-phase $C_2H_3O^+$ ions. Calculations have been carried out with polarization basis sets and with valence-electron correlation incorporated via Møller–Plesset perturbation theory terminated at third order. Geometries of equilibrium structures and transition structures have been determined by using analytical gradient techniques. Harmonic vibrational frequencies have been calculated in order to characterize stationary points in the potential energy surface and to allow for inclusion of zero-point effects in estimating relative energies. The lowest energy $C_2H_3O^+$ isomer is the acetyl cation, $CH_3CO^+$ (**1**). Another experimentally observed isomer, the 1-hydroxyvinyl cation $CH_2COH^+$, is found to lie 181 kJ mol$^{-1}$ above **1**, with a barrier to rearrangement (via successive 1,2-hydrogen shifts) of 287 kJ mol$^{-1}$. The calculations suggest that the third $C_2H_3O^+$ isomer observed in collisional activation mass spectrometry experiments is the oxiranyl cation, $\overline{CH_2CHO}^+$, lying 244 kJ mol$^{-1}$ above **1**, with a barrier to rearrangement (via ring-opening followed by a 1,2-hydrogen shift) of 85 kJ mol$^{-1}$. Of the other species examined, $CH_3OC^+$ and the ethynyloxonium cation, $CHCOH_2^+$, offer some prospect for experimental observation. The formylmethyl cation, $CH_2CHO^+$, and the 2-hydroxyvinyl cation, $CHCHOH^+$, are likely to collapse without activation energy to the acetyl cation and 1-hydroxyvinyl cation, respectively.

A number of recent experimental[1-7] and theoretical[8,9] studies have been aimed at determining the structures and, in some cases, relative energies of gaseous $C_2H_3O^+$ ions. The experimental work has been focused mainly on determining the site of protonation and the proton affinity of ketene ($CH_2CO$),[2-4] and, more recently, on investigating the structures of long-lived $C_2H_3O^+$ ions by means of collisional activation mass spectrometry.[5-7] Of the potential $C_2H_3O^+$ isomers that can be considered (**1–11** in Figure 1), only the acetyl cation (**1**) and the 1-hydroxyvinyl cation (**2**) are well characterized as being stable, observable species.[2,6] In addition, the results of a recent collisional activation study[7] indicate the existence of a third stable species. On the basis of its mechanism of formation, this isomer was postulated[7] to be either of structure **4** or **5**.

In previous theoretical work,[8,9] only a limited number of $C_2H_3O^+$ structures have been examined and no attempt has been made to determine barriers for interconversion of the various ions. The previous studies also suffered in that they were restricted to the single-configuration Hartree–Fock level (i.e., no account was taken of the effects of electron correlation) with small, nonpolarized basis sets. It was therefore deemed desirable to undertake the present systematic study of $C_2H_3O^+$ isomers and their intramolecular rearrangement pathways. Fully optimized geometries are used throughout, and, calculations with reasonably large, polarization basis sets including valence-electron correlation have been undertaken in order to obtain reliable relative energies. With the aid of the present results, a clearer understanding of the most recent experimental work[7] emerges.

## Method and Results

Standard ab initio molecular orbital calculations have been carried out by using a modified[10] version of the GAUSSIAN80 system of programs.[11] Stationary points in the singlet $C_2H_3O^+$ potential energy surface have been located at the Hartree–Fock (HF) level by using gradient optimization techniques[12] with the split-valence 4-31G basis set.[13] Harmonic vibrational frequencies have been determined at the HF/4-31G level in order to characterize stationary points as minima (equilibrium structures) or saddle points (transition structures) and also to allow for inclusion of the effects of zero-point vibrations in estimating relative energies. Improved energies have been obtained from higher level calculations that employ the dp-polarization 6-31G** basis set[14] and that incorporate valence-electron correlation via second-(MP2) and

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Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (kJ mol$^{-1}$) of Equilibrium Structures and Transition Structures[a]

| species | HF/4-31G | HF/6-31G** | MP2/6-31G** | MP3/6-31G** | ZPE |
|---|---|---|---|---|---|
| $CH_3CO^+$ (1) | −151.817 94 | −152.064 15 | −152.497 28 | −152.503 53 | 126.3 |
| $CH_2COH^+$ (2) | −151.760 40 | −151.995 23 | −152.417 56 | −152.433 16 | 122.5 |
| $CH_3OC^+$ (3) | −151.764 33 | −151.997 92 | −152.403 46 | −152.418 57 | 118.6 |
| $CH_2CHO^+$ (4) | −151.705 59 | −151.963 60 | −152.403 83 | −152.408 95 | 121.9 |
| $CH_2CHO^+$ (5) | −151.711 61 | −151.947 29 | −152.359 13 | −152.376 15 | 121.1 |
| $CHCOH_2{}^+$ (6) | −151.709 59 | −151.925 14 | −152.355 11 | −152.367 97 | 127.0 |
| $CHCHOH^+$ (7) | −151.708 05 | −151.940 22 | −152.343 58 | −152.364 56 | 119.0 |
| $CHCHOH^+$ (8) | −151.674 26 | −151.915 36 | −152.353 72 | −152.367 63 | 118.4 |
| $CH_2OCH^+$ (9) | −151.656 06 | | | | |
| $CCHOH_2{}^+$ (10) | −151.654 46 | | | | |
| TS 12, 5 → 1 | −151.694 80 | −151.940 33 | −152.370 02 | −152.380 29 | 111.8 |
| TS 13, 5 → 2 | −151.606 45 | −151.853 20 | −152.316 01 | −152.316 78 | 101.6 |
| TS 14, 5 → 4 | −151.705 56 | −151.954 06 | −152.383 64 | −152.390 71 | 118.0 |
| TS 15, 3 → 1 | −151.727 19 | −151.975 23 | −152.373 14 | −152.388 27 | 106.0 |
| TS 16, 4 → 3 | −151.574 12 | −151.847 34 | −152.295 20 | −152.306 38 | 111.2 |
| TS 17, 7 → 2 | −151.683 22 | −151.935 28 | −152.361 79 | −152.375 26 | 105.5 |
| TS 18, 7 → 6 | −151.594 34 | −151.826 14 | −152.275 93 | −152.282 76 | 101.9 |
| $CH_3{}^+$ [b] | −39.175 12 | −39.236 26 | −39.346 45 | −39.364 41 | 88.0 |
| CO[c] | −112.552 36 | −112.737 34 | −113.020 04 | −113.018 34 | 13.9 |
| $CH_2CO$[d] | −151.494 93[d] | −151.727 87[d] | −152.162 06[d] | −152.167 77[d] | 90.4 |

[a] Based on HF/4-31G geometries. [b] $r_e$(C–H) = 1.076 Å. [c] $r_e$(C–O) = 1.128 Å. [d] Reference 29.

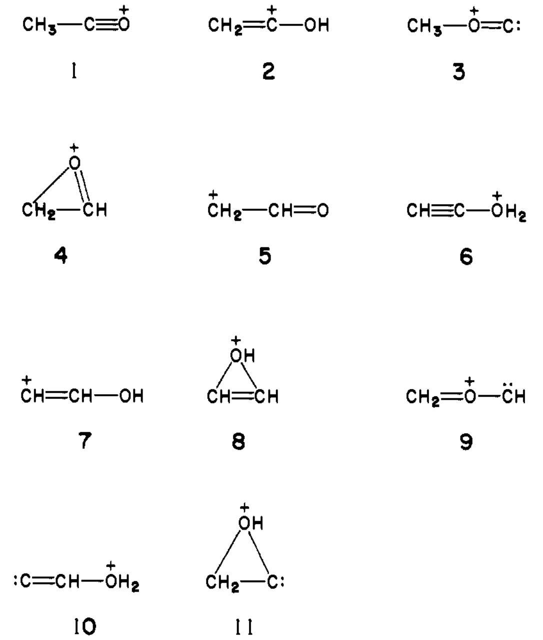


Figure 1. Possible isomeric $C_2H_3O^+$ structures.

third-(MP3) order Møller–Plesset perturbation theory.[15]

Geometries optimized with the 4-31G basis set are displayed within the text. Bond lengths are given in angstroms and bond angles in degrees. Total energies and zero-point vibrational energies are shown in Table I, while relative energies are given in Table II. Structures are classified in Tables I and II as equilibrium structures or as transition structures on the basis of the vibrational analysis carried out at the HF/4-31G level. The nature of some of these structures is modified at higher levels of theory as described in the text. Unless otherwise stated, energy comparisons within the text refer to MP3/6-31G** values with the addition of a contribution for zero-point vibrations. Since HF calculations are known[16,17] to overestimate vibrational frequencies by ~10%, the zero-point vibrational contributions to relative energies were obtained by scaling the calculated zero-point energies by a factor of 0.9. Experimental heats of reaction are based on $\Delta H_f{}^\circ{}_{298}$ values.

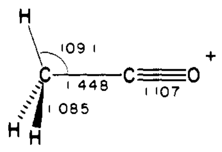
Table II. Calculated Relative Energies (kJ mol$^{-1}$) of $C_2H_3O^+$ Species

| species | HF/4-31G | HF/6-31G** | MP2/6-31G** | MP3/6-31G** | MP3/6-31G**[a] |
|---|---|---|---|---|---|
| $CH_3CO^+$ (1) | 0 | 0 | 0 | 0 | 0 |
| $CH_2COH^+$ (2) | 151 | 181 | 209 | 185 | 181 |
| $CH_3OC^+$ (3) | 141 | 174 | 246 | 223 | 216 |
| $CH_2CHO^+$ (4) | 295 | 264 | 245 | 248 | 244 |
| $CH_2CHO^+$ (5) | 279 | 307 | 363 | 334 | 330 |
| $CHCOH_2{}^+$ (6) | 284 | 365 | 373 | 356 | 357 |
| $CHCHOH^+$ (7) | 289 | 325 | 404 | 365 | 358 |
| $CHCHOH^+$ (8) | 377 | 391 | 377 | 357 | 350 |
| $CH_2OCH^+$ (9) | 425 | | | | |
| $CCHOH_2{}^+$ (10) | 429 | | | | |
| TS 12, 5 → 1 | 323 | 325 | 334 | 324 | 311 |
| TS 13, 5 → 2 | 555 | 554 | 476 | 490 | 468 |
| TS 14, 5 → 4 | 295 | 289 | 298 | 296 | 289 |
| TS 15, 3 → 1 | 238 | 233 | 326 | 303 | 284 |
| TS 16, 4 → 3 | 640 | 569 | 531 | 518 | 504 |
| TS 17, 7 → 2 | 354 | 338 | 356 | 337 | 318 |
| TS 18, 7 → 6 | 587 | 625 | 581 | 580 | 558 |
| $CH_3{}^+$ + CO | 237 | 238 | 343 | 317 | 295 |
| $CH_2CO$ + $H^+$ | 848 | 883 | 880 | 882 | 849 |

[a] MP3/6-31G** values with zero-point contribution (see text).

## Discussion

**Geometries and Relative Energies: Acetyl Cation (1).** The acetyl cation (1) is an important fragment ion in the mass spectra of many oxygen-containing organic molecules. The HF/4-31G optimum structure of 1 has been reported previously,[18] and is



1 ($C_{3v}$)

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similar to that obtained by Yarkony and Schaefer (YS)[9] in a Hartree–Fock study using a double-$\zeta$ basis set.

We find dissociation of **1** into a methyl cation and carbon monoxide

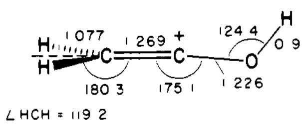
$$CH_3CO^+ \rightarrow CH_3^+ + CO \qquad (1)$$

to proceed with zero reverse activation energy and to require 295 kJ mol$^{-1}$. On the basis of literature values of the heats of formation of $CH_3CO^+$ (670 kJ mol$^{-1}$),[2,4,19] $CH_3^+$ (1092 kJ mol$^{-1}$),[20] and CO (−111 kJ mol$^{-1}$),[20] reaction 1 would be expected to be endothermic by 311 kJ mol$^{-1}$. On the other hand, a more recent value[21] of $\Delta H_f(CH_3CO^+)$ (640 kJ mol$^{-1}$) leads to an endothermicity of 341 kJ mol$^{-1}$.

It is well established[2,4] that, with weak proton donors, ketene protonates preferentially on the methylene carbon to yield **1**. Earlier measurements[2,4,19] of the proton affinity of ketene gave values in the range 812–820 kJ mol$^{-1}$. The most recent values of the heats of formation of ketene (−47.7 kJ mol$^{-1}$)[22] and of $CH_3CO^+$ (640 kJ mol$^{-1}$)[21] together with the established value for $H^+$ (1530 kJ mol$^{-1}$) give rise to a proton affinity for ketene of 842 kJ mol$^{-1}$. Our calculated value is 849 kJ mol$^{-1}$.

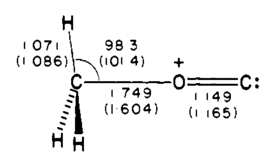
**1-Hydroxyvinyl Cation (2).** Experimental work[2,6] has shown that, in addition to protonation on the methylene carbon, reaction of ketene with strong acids such as $CH_5^+$ may lead to protonation on the oxygen atom, yielding $CH_2COH^+$ (**2**). C-protonation has been found[2] to be favored by ~75 ± 30 kJ mol$^{-1}$; this represents an experimental estimate of the energy difference between **1** and **2**. A collisional activation study[6] offers evidence that **2** may also be formed from fragmentation of the ethanol radical cation.

The HF/4-31G structure of **2** is similar to that obtained by YS, but the C–O length is significantly shorter than that obtained in another study[23] employing a minimal basis set. The 1-hydroxyvinyl cation (**2**) is predicted to lie 181 kJ mol$^{-1}$ above **1**, which is at variance with the energy difference from ICR studies[2] noted above. However, more recent experimental estimates[21] of the heats of formation of **1** (640 kJ mol$^{-1}$) and **2** (820 kJ mol$^{-1}$) yield an energy difference of 180 kJ mol$^{-1}$, in excellent agreement with our calculated result.



2 ($C_s$)

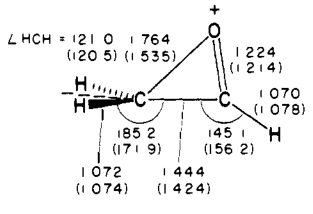
$CH_3OC^+$ (**3**). We are unaware of any previous experimental or theoretical study of the $CH_3OC^+$ ion (**3**). Examination of the HF/4-31G structure of **3** shows that the bond between the methyl carbon and the oxygen atom is quite long at 1.749 Å, which suggests that at this level **3** should be viewed as a complex of $CH_3^+$ and CO. The binding energy with respect to dissociation into these fragments is calculated to be 79 kJ mol$^{-1}$. Hartree–Fock calculations are known in some cases to lead to poor descriptions of such complexes,[24] and thus the structure of **3** was reoptimized at the MP2/6-31G* level, yielding the geometrical parameters shown in parentheses. The C–O bond length, although shortened somewhat from the HF/4-31G value, is still found to be quite long (1.604 Å).



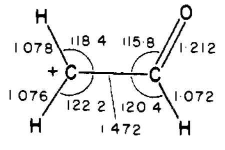
3 ($C_{3v}$)

$CH_3OC^+$ (**3**) is found to be the third lowest in energy of the $C_2H_3O^+$ ions examined, lying 216 kJ mol$^{-1}$ above $CH_3CO^+$ (**1**). This value may be compared with an energy difference of 157 kJ mol$^{-1}$ in the analogous $HOC^+$–$HCO^+$ system.[25]

**Oxiranyl Cation (4) and Formylmethyl Cation (5).** In a recent collisional activation study,[7] it was found that certain precursor molecules give mixtures of two long-lived $C_2H_3O^+$ ions upon fragmentation. These ions were postulated to be the acetyl cation (**1**) and either the cyclic structure $\overline{CH_2CHO}^+$ (**4**) or the formylmethyl cation $CH_2CHO^+$ (**5**); **4** and **5** could not be differentiated in this experiment. It has also been proposed[26] that the cyclic ion **4** may be formed directly by $\alpha$ cleavage of ionized aliphatic epoxides.



4 ($C_s$)

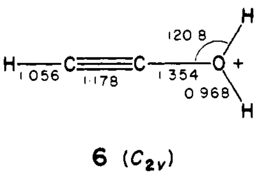


5 ($C_s$)

Both **4** and **5** are calculated to be minima in the HF/4-31G potential surface, with the open structure **5** lying slightly lower in energy than the cyclic ion **4** (however, see below). At this level the profile for ring-opening **4** → **5** is found to be extremely flat, and this is reflected in an exaggerated $H_2C$–O bond length in **4** (1.764 Å). Full optimization of the geometry of **4** with the d-polarization 6-31G* basis set yields the structure shown in parentheses; this structure has a much shorter C–O bond (1.535 Å) and is thought to be the more accurate of the two given (YS obtain a C–O length of 1.570 Å in their double-$\zeta$ optimization). However, even though the structural changes are significant, preliminary calculations at the MP2/6-31G* level indicate that the energy of **4** relative to **1** is quite insensitive to the choice of either 4-31G or 6-31G* geometries (reflecting the flatness of the potential surface in this region), and thus for consistency the 4-31G structure has been employed in subsequent calculations.

Our best calculations predict that **4** lies 244 kJ mol$^{-1}$ above **1** (cf. the YS estimate of 293 kJ mol$^{-1}$) and that **5** lies 330 kJ mol$^{-1}$ above **1** (cf. previous theoretical results[8,9] of 273 and 268 kJ mol$^{-1}$ obtained at lower levels and an empirical estimate[27] of ~100 kJ mol$^{-1}$ based on an additivity scheme).

**Ethynyloxonium Cation (6).** There have been no previous studies of the ethynyloxonium cation (**6**). This ion is calculated to lie 357 kJ mol$^{-1}$ above the acetyl cation (**1**).



6 ($C_{2v}$)

**2-Hydroxyvinyl Cation (7) and Protonated Oxirene (8).** The 2-hydroxyvinyl cation (**7**) and protonated oxirene (**8**) have been

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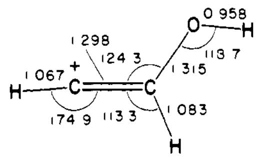
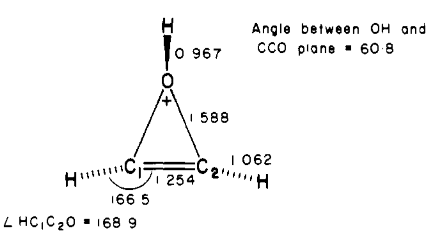
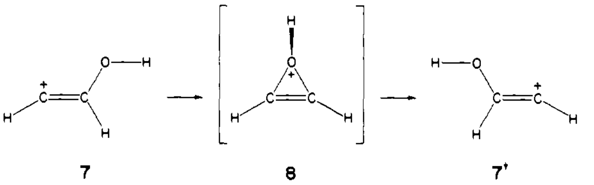


**7** ($C_s$)



**8** ($C_s$)

the subject of two previous (but lower level) theoretical studies.[23,28] In contrast to the earlier work,[28] the anti conformer of 7 is found to be lower in energy than the syn conformer (by ~11 kJ mol$^{-1}$) at the HF/4-31G level. The cyclic structure **8** is found not to be a minimum in the HF/4-31G surface but rather represents the transition structure in this surface for the degenerate hydroxyl shift **7** → **7′** (eq 2); this is reflected in the long C–O bonds in **8**.

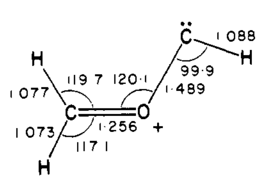


(2)

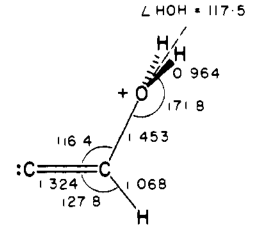
**7** **8** **7′**

At the HF/4-31G level, this rearrangement is calculated to require 89 kJ mol$^{-1}$ (cf. previous estimates[23,28] of 104 and 91 kJ mol$^{-1}$). Note, however, that at higher levels the bridged structure **8** falls slightly lower in energy than the open form **7**, our best estimates of the energies of **7** and **8** being 358 and 350 kJ mol$^{-1}$ above **1**, respectively. This effect would probably be accentuated by reoptimization of the geometries at higher levels, suggesting that the cyclic form **8** may indeed be the preferred of these two structures.

**Other Structures Examined.** Two other minima were found in the HF/4-31G surface. These are the carbenoid species **9** and **10** (best conformations shown). The energies of **9** and **10** were



**9** ($C_s$)



**10** ($C_s$)

found to be high at the HF/4-31G level (425 and 429 kJ mol$^{-1}$ above **1**, respectively), and hence these species are not examined further in this study.

Attempts to optimize the structure of the cyclic species **11** (Figure 1) led to ring-opening via C–O bond cleavage to give the 1-hydroxyvinyl cation (**2**).

**Intramolecular Rearrangements: Rearrangements Involving the Formylmethyl Cation (5).** A number of rearrangements involving the formylmethyl cation (**5**) have been examined. These are shown schematically in Figure 2.

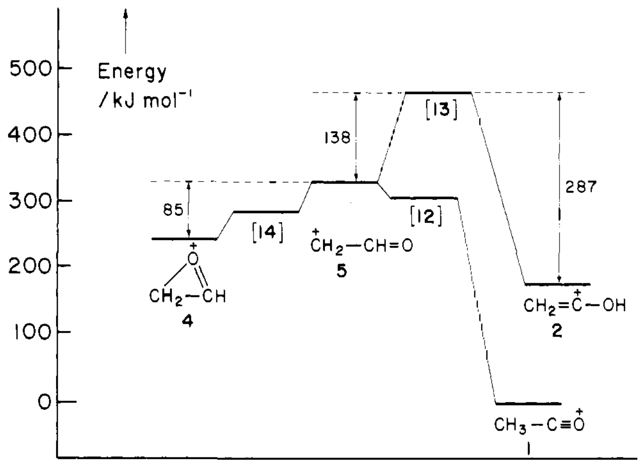


**Figure 2.** Schematic energy profile for rearrangements involving the formylmethyl cation (**5**).

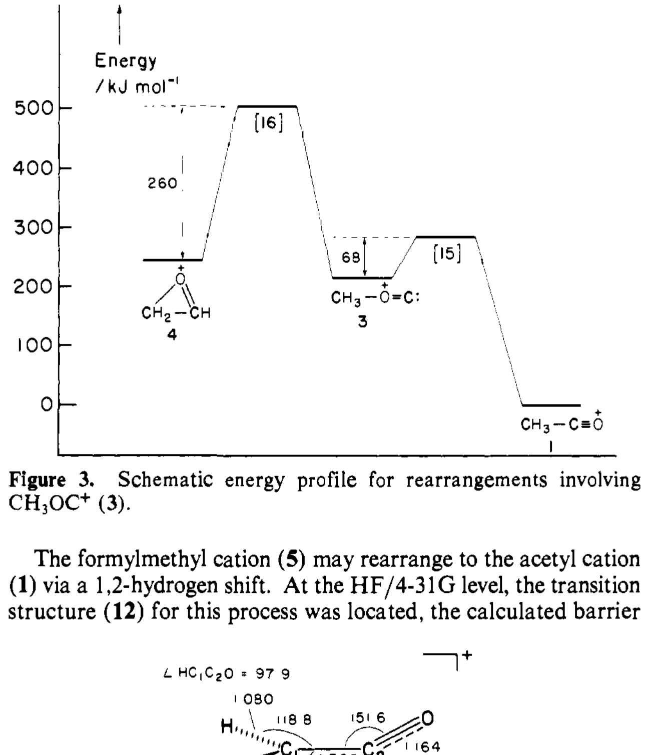
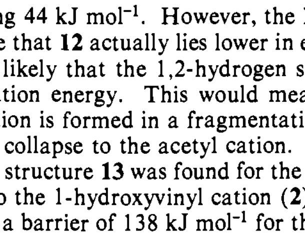


**Figure 3.** Schematic energy profile for rearrangements involving $CH_3OC^+$ (**3**).

The formylmethyl cation (**5**) may rearrange to the acetyl cation (**1**) via a 1,2-hydrogen shift. At the HF/4-31G level, the transition structure (**12**) for this process was located, the calculated barrier for **5** → **1** being 44 kJ mol$^{-1}$. However, the higher level calculations indicate that **12** actually lies lower in energy than **5**, and it is therefore likely that the 1,2-hydrogen shift **5** → **1** occurs without activation energy. This would mean that if the formylmethyl cation is formed in a fragmentation process, it may spontaneously collapse to the acetyl cation.



**12** ($C_1$→$C_s$)

A transition structure **13** was found for the 1,2-hydrogen shift converting **5** to the 1-hydroxyvinyl cation (**2**). The best calculations predict a barrier of 138 kJ mol$^{-1}$ for this rearrangement.

In keeping with previous experience,[29] we have been unable to locate in this study transition structures for 1,3-hydrogen shifts between terminal atoms in linear systems (in this case, **2** → **1** and

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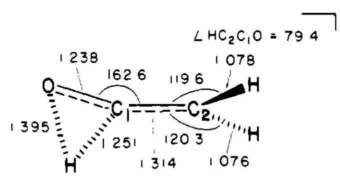
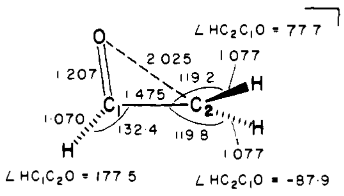


**13** ($C_1$)

**6** → **2**). An alternative to a direct 1,3-shift is two consecutive 1,2-shifts. In the case of the rearrangement of the 1-hydroxyvinyl cation (**2**) to the acetyl cation (**1**), such a pathway would have **5** as an intermediate, i.e., **2** → **5** → **1**. The activation energy for **2** → **1** via such a mechanism (given by the energy of **13** above **2**) is quite high (287 kJ mol$^{-1}$).

Ring closure in **5** yields the oxiranyl cation **4**. As mentioned above, at the HF/4-31G level the open structure **5** is predicted to lie lower in energy than the cyclic form **4** with virtually no barrier to ring-opening **4** → **5** (via transition structure **14**). However, the higher level calculations indicate that **4** lies 85 kJ mol$^{-1}$ lower in energy than **5** and that, in addition, the HF/4-31G transition structure **14** also lies lower than **5**. This suggests that **5** may also spontaneously collapse via ring closure to **4**.

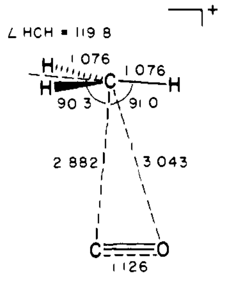


**14** ($C_1$)

As a consequence of the flatness of the HF/4-31G potential energy surface in the region of structures **4** and **14**, we were unable to locate transition structures for the direct rearrangements **4** → **1** and **4** → **2**, both of which involve a 1,2-hydrogen shift with concomitant ring-opening via C–O bond cleavage. However, if these reactions are assumed to occur in a stepwise manner with ring-opening being the initial process (i.e., **4** → **5** → **1** and **4** → **5** → **2**), the barriers can be estimated to be 85 and 224 kJ mol$^{-1}$, respectively.

**Rearrangements Involving $CH_3OC^+$ (3).** Two rearrangements involving $CH_3OC^+$ (**3**) have been examined. These are shown schematically in Figure 3.

A transition structure (**15**) was located for the methyl shift converting $CH_3OC^+$ (**3**) into the acetyl cation (**1**). The $CH_3OC^+$ → $CH_3CO^+$ rearrangement is isoelectronic with $CH_3NC$ → $CH_3CN$, a rearrangement that has been examined in a number of ab initio studies.[30-34] As is found[34] in the $CH_3NC$ → $CH_3CN$ system, the transition structure **15** has $C_s$ symmetry with the in-plane methyl hydrogen eclipsing the heteroatom (rather than the other carbon atom). However, the $CH_3NC$ → $CH_3CN$ transition structure has $C_{methyl}$–C and $C_{methyl}$–N lengths (1.740 and 1.898 Å, respectively)[34] typical of partially broken bonds whereas **15** is found to have long $C_{methyl}$–C and $C_{methyl}$–O bonds (2.882 and 3.043 Å, respectively). The barrier to the rearrangement $CH_3NC$ → $CH_3CN$ is large (~171 kJ mol$^{-1}$).[34] In contrast, the barrier for **3** → **1** is quite low (68 kJ mol$^{-1}$), due primarily to the fact that **3** lies high in energy relative to **1**.



**15** ($C_s$)

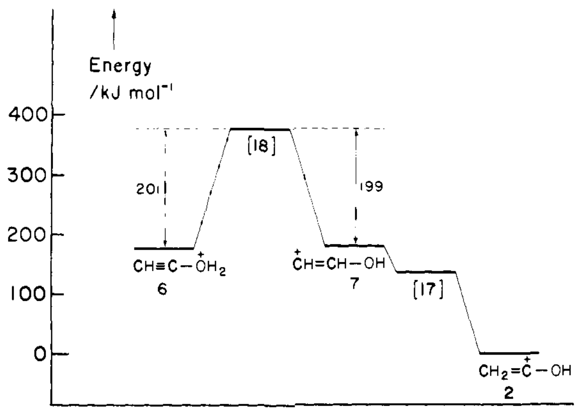
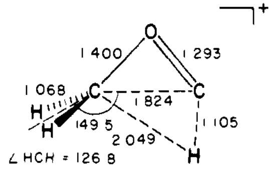


**Figure 4.** Schematic energy profile for rearrangements involving the 2-hydroxyvinyl cation (**7**).

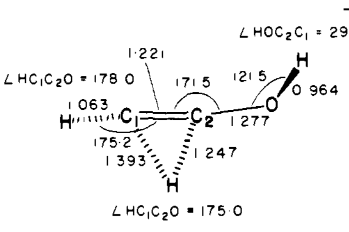
A transition structure (**16**) was found for the rearrangement **4** → **3** (involving ring-opening via C–C bond cleavage with a concomitant 1,2-hydrogen shift). The barrier is predicted to be high (260 kJ mol$^{-1}$).



**16** ($C_s$)

**Rearrangements Involving the 2-Hydroxyvinyl Cation (7).** A number of rearrangements involving the 2-hydroxyvinyl cation (**7**) have been examined. These are shown schematically in Figure 4.

The 2-hydroxyvinyl cation (**7**) may rearrange to the 1-hydroxyvinyl cation (**2**) via a 1,2-hydrogen shift across the C–C double bond. Although a transition structure (**17**) was located at the HF/4-31G level, the higher level calculations again indicate a process that is likely to have no barrier, i.e., **7** may collapse spontaneously to **2**.



**17** ($C_1$)

The rearrangement **7** → **6**, occurring via a 1,2-hydrogen shift and transition structure **18**, was also examined. The barrier is predicted to be 199 kJ mol$^{-1}$.

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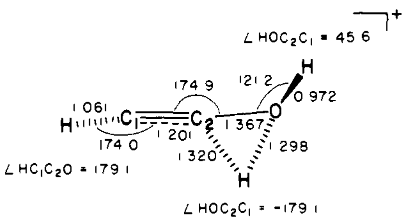


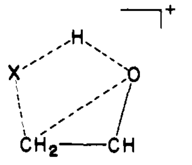
**18** ($C_1$)

As mentioned earlier, the transition structure for the 1,3-hydrogen shift **6** → **2** could not be found. The activation energy for this rearrangement via consecutive 1,2-hydrogen shifts **6** → **7** → **2** is predicted to be 201 kJ mol$^{-1}$.

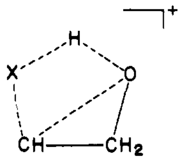
**Comparison with Collisional Activation Results.** The most recent experimental work on the $C_2H_3O^+$ system, a collisional activation study by Terlouw, Heerma, and Holmes,[7] can be rationalized with the aid of the present results.

These workers found that, as expected, precursors containing the $CH_3CO$– moiety yield on fragmentation the acetyl cation (**1**) by a simple bond cleavage (Scheme I, path A). Contrary to expectations, however, the $C_2H_3O^+$ ions from methyl vinyl ether, ethyl vinyl ether, and cyclobutanol were also found to be of structure **1**. These precursors would have been expected to yield ions with the $CH_2CHO^+$ structure (**5**), produced by loss of R· from initially formed $CH_2{=}CHOR^{+\cdot}$ ions (R = $CH_3$, $C_2H_5$, and H, respectively). Our calculations show, however, that **5** collapses with little or no activation energy to **1** and are therefore consistent with the experimental observation of **1** from these precursors (Scheme I, path B).

For two molecules, 1,3-dichloropropan-2-ol, and 2,2-dichloroethanol, the $C_2H_3O^+$ ions produced were found[7] to be distinct from the acetyl cation (**1**) (as well as from the well-established[6] 1-hydroxyvinyl cation (**2**)). In these cases, ionization followed by fragmentation is envisaged[7] to lead to intermediates of general structure $XCH_2C^+HOH$ or $XC^+HCH_2OH$, respectively. We would propose that 1,3-elimination of HX from such intermediates involves transition structures (**19a** or **19b**, respectively) in which the terminal carbon and oxygen atoms are in relatively close proximity; the geometry of such transition structures is favorable for concomitant ring closure and the formation of the oxiranyl cation (**4**) (Scheme I, path C).



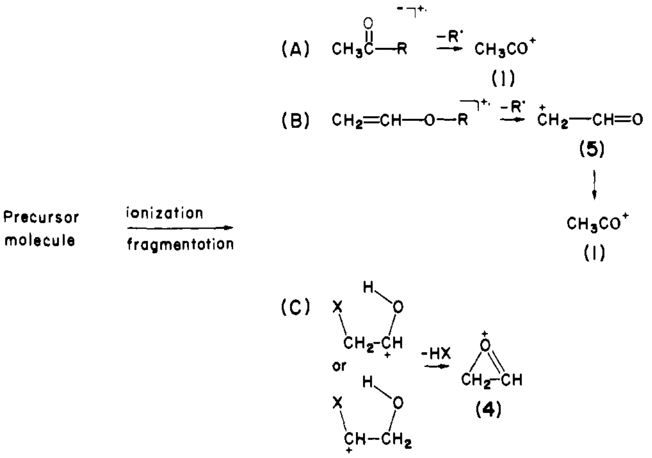
**19a**



**19b**

The general scheme proposed here is consistent with Scheme I of ref 7 and allows a number of precursors (e.g., ethylene glycol, 2-fluoroethanol, and 2-chloroethanol) to fragment via competing pathways (B and C of Scheme I), leading to a mixture of $C_2H_3O^+$ ions **1** and **4**.

Scheme I



Finally, we note that in a study[1] of the fragmentation reactions of 2-buten-1-ol it was proposed that 1,3-loss of the ethyl radical from the molecular ion leads to a $C_2H_3O^+$ ion of structure **4**; this corresponds to path C in Scheme I with X = $CH_3CH$.

## Conclusions

(i) The lowest energy $C_2H_3O^+$ isomer is the acetyl cation (**1**).

(ii) Our results support the existence of the 1-hydroxyvinyl cation (**2**) as a stable $C_2H_3O^+$ ion. This isomer is predicted to lie 181 kJ mol$^{-1}$ above **1**, with a barrier to rearrangement (via consecutive 1,2-hydrogen shifts **2** → **5** → **1**) of 287 kJ mol$^{-1}$.

(iii) $CH_3OC^+$ (**3**) lies 216 kJ mol$^{-1}$ above **1** and is bound by 79 kJ mol$^{-1}$ with respect to dissociation into $CH_3^+$ + CO. The 1,2-methyl shift converting **3** to **1** is calculated to require an activation energy of 68 kJ mol$^{-1}$.

(iv) It is likely that the $C_2H_3O^+$ ions observed in a recent collisional activation study[7] are the acetyl cation (**1**) and the oxiranyl cation (**4**). The latter isomer is predicted to lie 244 kJ mol$^{-1}$ above **1**, with a barrier to rearrangement (via a mechanism **4** → **5** → **1** involving ring-opening followed by a 1,2-hydrogen shift) of 85 kJ mol$^{-1}$.

(v) Although the ethynyloxonium cation (**6**) lies somewhat higher in energy (357 kJ mol$^{-1}$ above **1**), it offers some prospect for experimental observation because the lowest pathway for rearrangement (via successive 1,2-hydrogen shifts **6** → **7** → **2**) requires substantial activation energy (201 kJ mol$^{-1}$).

(vi) The formylmethyl cation (**5**) is predicted to collapse without activation energy to either **1** or **4**. Similarly, the 2-hydroxyvinyl cation (**7**) collapses without a barrier to the 1-hydroxyvinyl cation (**2**).

**Registry No. 1**, 15762-07-9; **2**, 62581-51-5; **3**, 83967-74-2; **4**, 57789-76-1; **5**, 41084-88-2; **6**, 83967-75-3; **7**, 63812-38-4; **8**, 63812-37-3; **9**, 83967-76-4; **10**, 83967-77-5.