Structures and Stabilities of $C_3H_6O^{+\cdot}$ Isomers. An ab Initio Molecular Orbital Study

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Abstract: Seventeen $C_3H_6O^{+\cdot}$ isomers, including the molecular ions of all known isomers of the neutral C_3H_6O parents, have been studied with the aid of ab initio molecular orbital theory. Calculations have been performed with minimal (STO-3G) and split-valence (4-31G) basis sets using the restricted Hartree-Fock (RHF) procedure. All geometries have been fully optimized subject to specified symmetry constraints at the minimal basis set level and relative energies have been calculated with the larger basis set. Apart from the well-established isomers, a number of additional low-energy isomers have been identified. Preliminary ICR experimental studies provide support for the existence of some of these species.

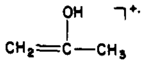
Introduction

Over the past 10 years, structural isomerism in gas-phase cations has received wide attention.[1] There have been numerous studies of isomeric systems utilizing mass spectrometric techniques, including several investigations of the $C_3H_6O^{+\cdot}$ isomers.[2-14]

In recent papers[15-17] we have reported theoretical studies of the $CH_2O^{+\cdot}$ and the $C_2H_4O^{+\cdot}$ systems, and were able to identify a number of low-energy isomers, one of which (the C···C ring-opened ethylene oxide ion) had only recently been postulated[18] and whose existence has subsequently been verified[19] by ICR spectrometry. In the present study, we have examined seven $C_3H_6O^{+\cdot}$ isomers (**4-7, 13, 15,** and **16**) which correspond to the molecular ions of known neutral C_3H_6O isomers and ten additional $C_3H_6O^{+\cdot}$ isomers (**1-3, 8-12, 14,** and **17**), two of which have previously been observed as stable gas-phase ions.

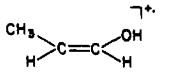
As stated, the $C_3H_6O^{+\cdot}$ isomers have received considerable attention from experimentalists, who have been concerned with identifying and distinguishing the various isomers. Ion cyclotron resonance studies[2-4] established that the acetone radical cation (**4**) and its enol isomer (**1**), generated from suitable precursors, are distinct, noninterconverting species, but no evidence was found for the symmetric oxonium ion (**9**), which had been proposed to result from a double McLafferty rearrangement in alkanones. ICR studies[10,12,13] of the methyl vinyl ether radical cation (**5**) identified ion/molecule reactions characteristic of this ion, and in an ICR study of cyclopropanol[14] the molecular ion (**16**) was assumed to retain the cyclopropanol structure. The question of whether **1** and **4** interconvert was also examined by labeling and metastable ion studies,[5,8] which confirmed the ICR result. Metastable analysis of the decomposition of the molecular ions of propylene oxide, propanal, and trimethylene oxide showed that they were distinct species. It must be noted that metastable ion studies are of short-lived decomposing ions (10^{-5}-10^{-6} s), whereas ICR experiments involve stable ions of relatively long lifetimes ($>10^{-3}$ s). A further method of distinguishing between isomeric gas-phase ions is by their collisional activation spectra. With this technique seven $C_3H_6O^{+\cdot}$ isomers, formed from a number of precursors, were identified[6,11] as discrete species. They were the molecular ions of acetone (**4**), propanal (**6**), methyl vinyl ether (**5**), trimethylene oxide (**13**), and propylene oxide (**15**), plus the enol isomers **1** and **2** and/or **3**. A notable omission from this study was the cyclopropanol molecular ion (**16**). The molecular ion of allyl alcohol (**7**) was reported[11] to isomerize to the enol ion **2**, presumably via a 1,3-hydrogen shift.

There are several reasons for undertaking the present theoretical study of the $C_3H_6O^{+\cdot}$ system.



$CH_2{=}\overset{OH}{C}{-}CH_3 \;\rceil^{+\cdot}$

1



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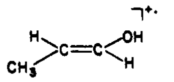

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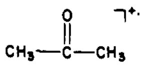


$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \;\rceil^{+\cdot}$

4

$CH_2{=}CH{-}O{-}CH_3 \;\rceil^{+\cdot}$

5

$CH_3{-}CH_2{-}CH{=}O \;\rceil^{+\cdot}$

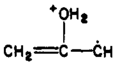
6

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

7

$CH_3{-}C{-}O{-}CH_3 \;\rceil^{+\cdot}$

8



$CH_2{=}\overset{^{+}OH_2}{C}{-}\dot{C}H_2$

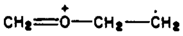
9

$CH_3{-}CH{-}O{-}CH_2 \;\rceil^{+\cdot}$

10

$CH_3{-}CH_2{-}C{-}OH \;\rceil^{+\cdot}$

11



$CH_2{=}\overset{+}{O}{-}CH_2{-}\dot{C}H_2$

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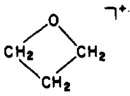

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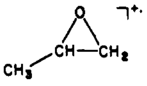
$CH_3{-}CH_2{-}O{-}CH \;\rceil^{+\cdot}$

14



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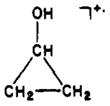

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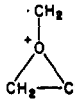

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(i) In the first place, it extends our previous studies of the $CH_2O^{+\cdot}$ and $C_2H_4O^{+\cdot}$ systems.

(ii) It enables the detailed structural parameters of the various $C_3H_6O^{+\cdot}$ isomers to be determined. These are not yet accessible experimentally but provide valuable insight into the properties of the ions.

(iii) Since thermochemical information for the $C_3H_6O^{+\cdot}$ system is quite fragmentary, it is very useful to obtain a complete set of theoretical relative energies.

(iv) From these energy calculations, low-energy isomers may be identified which have not hitherto been observed experimentally.

Methods and Results

Standard LCAO-SCF-MO calculations were carried out using a modified version of the GAUSSIAN 70 system of programs,[20,21] employing a restricted Hartree-Fock (RHF) approach[22] with the STO-3G[23] and 4-31G[24] basis sets.

In our previous study of the $C_2H_4O^{+\cdot}$ isomers,[16] we per-

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Table I. Calculated Total Energies (hartrees) and Relative Energies (kJ mol^{-1}) for the $C_3H_6O^{+\cdot}$ Isomers[a]

isomer[b]	symmetry	state	RHF/STO-3G//RHF/STO-3G energy total	RHF/STO-3G//RHF/STO-3G energy rel	RHF/4-31G//RHF/STO-3G energy total	RHF/4-31G//RHF/STO-3G energy rel	exptl[c] $\Delta H_f°(298)$
1	C_s	$^2A''$	−189.296 15	0	−191.374 88	0	*d*
2	C_s	$^2A''$	−189.289 51	17.4	−191.369 91	13.0	*d*
3	C_s	$^2A''$	−189.289 51	17.4	−191.369 15	15.0	*d*
4	C_{2v}	$^2B_2$	−189.323 83	−72.7	−191.367 15	20.3	719
5	C_s	$^2A''$	−198.284 72	30.0	−191.354 51	53.5	*d*
6	C_s	$^2A'$	−189.295 94	0.6	−191.339 49	92.9	770
7	C_s	$^2A''$	−189.234 05	163.0	−191.333 94	107.5	*d*
8	C_s	$^2A'$	−189.280 47	41.2	−191.332 96	110.1	*d*
9	C_{2v}	$^2A_2$	−189.230 46	172.5	−191.332 54	111.2	*d*
10	C_s	$^2A'$	−189.273 14	60.4	−191.332 26	111.9	*d*
11	C_s	$^2A'$	−189.268 85	71.7	−191.328 02	123.0	*d*
12	C_s	$^2A'$	−189.250 88	118.9	−191.318 70	147.5	*d*
13	$C_s \rightarrow C_{2v}$	$^2B_1$	−189.317 90	−57.1	−191.314 95	157.3	852
14	C_s	$^2A'$	−189.254 01	110.6	−191.308 69	173.8	*d*
15	C_1	^2A	−189.283 11	34.2	−191.296 21	206.5	893
16	C_s	$^2A''$	−189.251 76	116.5	−191.287 50	229.4	*d*
17	$C_1 \rightarrow C_s$	$^2A'$	−189.249 25	123.1	−191.280 99	246.5	*d*

[a] Experimental heats of formation are listed for comparison. [b] For geometries, see text. [c] From ref 36. [d] Not available. See, however, ref 46.

formed geometry optimizations with both STO-3G and 4-31G basis sets and both RHF and UHF procedures. The results of that study suggest that geometry optimization using the RHF procedure and the STO-3G basis set should generally be satisfactory for obtaining structural information for radical cations of the type examined here. The calculated structures are likely, of course, to reflect some of the known shortcomings of the STO-3G method,[25] e.g., underestimation of the bond angles at oxygen atoms and failure to detect the small ring puckering of four-membered rings,[26] but for the most part we shall not be concerned with such details in the present study.

In order to obtain improved estimates of relative energies, single calculations have been carried out with the 4-31G basis set at the STO-3G optimized geometries (denoted RHF/4-31G//RHF/STO-3G). Again, in our previous study on the $C_2H_4O^{+\cdot}$ isomers, we found that the use of STO-3G optimized structures in such energy comparisons yielded results very similar to those obtained with 4-31G optimized structures (mean absolute deviation 2 kJ mol^{-1}). The difference between the 4-31G results and the more accurate 6-31G* relative energies was somewhat greater (mean absolute deviation 20 kJ mol^{-1}) but there was no qualitative disagreement between the two sets of results; i.e., the energy ordering of the 11 isomers studied was identical at the two levels, and this lends confidence to our use of 4-31G energies here. Unless otherwise noted, all energy comparisons in this paper refer to 4-31G values.

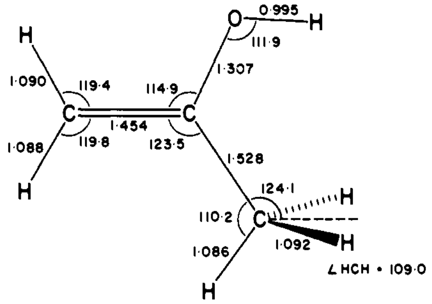
Optimized geometries are presented in the Discussion while corresponding total and relative energies are listed in Table I. Throughout this paper, bond lengths are in ångstroms and bond angles in degrees.

ICR experiments were carried out on a Dynaspec ICR-9-R instrument at 20 eV in the drift mode using electron energy modulation and emission currents of 0.01-0.04 μA. Samples were introduced via a dual inlet system which allowed individual variation of the relative sample gas pressures. Total operating pressure in the ICR cell was 1-2 × 10^{-5} Torr as measured by the ion pump current. The cell and inlet systems were maintained at ambient temperature. All ion/molecule reaction sequences were confirmed by double-resonance experiments.

The compounds used were either obtained commercially (dioxane, propylene oxide, trimethylene oxide, and acetonitrile) or synthesized by published procedures (4-methyl-1,3-dioxolane[27]). All compounds were purified by distillation or preparative GC before use.

Discussion

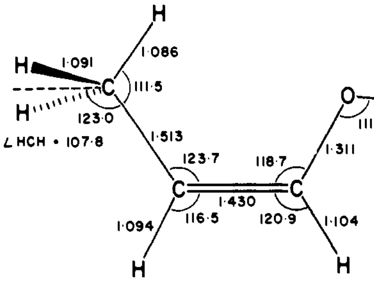
$CH_2{=}C(OH)CH_3^{+\cdot}$ (1). For the optimization of the 1-propen-2-ol radical cation, an initial structure based on the optimized structure of the vinyl alcohol radical cation[16] was chosen. The geometry of **1** was optimized in the conformation shown, imposing C_s symmetry only. This isomer, which is the enol tautomer of the acetone radical cation, is found to be the most stable $C_3H_6O^{+\cdot}$ isomer. This is consistent with experimental[28] and theoretical[15,16] results for the $C_2H_4O^{+\cdot}$ isomers, where the enol isomer was also found to be the most stable radical cation. We find that in **1** an electron has been removed from the π-electron system of 1-propen-2-ol, resulting in elongation of the C═C double bond and a shortening of the C—O bond, similar to the finding[16] for vinyl alcohol. The parent neutral compound, 1-propen-2-ol, has been identified as a transient species (in solution) by CIDNP ^1H and ^{13}C NMR spectroscopy.[29,30]



1

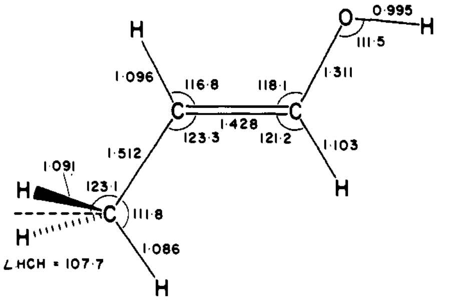
Unfortunately, no accurate heat of formation for ion **1** can be calculated. Estimates of the ionization potential of **1** range from 8.2[31] to 9.1-9.4 eV[32] with a "best" value of 8.75 eV,[33] while the most recent measurement of the $\Delta H_f°$ for the parent neutral $CH_3C(OH)CH_2$ puts it 13.9 ± 2 kJ mol^{-1} (58.2 ± 8.4 kJ mol^{-1}) above that of acetone (−217.57 kJ mol^{-1}).[34] From these, an approximate value of 685 kJ mol^{-1} is obtained for the $\Delta H_f°(298)$ for **1** but the uncertainty is so great that we prefer not to include this value in Table I (see, however, ref 47).

$CH_3CH{=}CHOH^{+\cdot}$ (**2** and **3**). For 1-propen-1-ol radical cation, geometric isomers corresponding to the methyl group being cis (**2**) or trans (**3**) to the hydroxyl group are possible and both have been examined. As for **1**, the hydroxylic hydrogen was chosen anti to the double bond, by analogy with the



2

structure of the vinyl alcohol radical cation. Both **2** and **3** were optimized subject to C_s symmetry constraints. A slightly lower energy (by 2.0 kJ mol^{-1}) is found for **2.** Isomers **2** and **3** have the same electronic states as **1,** with one electron being removed from the π-electron system of the neutral parent. The geometry of the enol moiety in **1–3** and the vinyl alcohol radical cation is very similar. The energy of **2** relative to **1** is only 13 kJ mol^{-1} (Table I). This energy difference is due to the dependence of the substituent effect for a methyl group on its position in the vinyl alcohol radical cation. Thus substitution by a methyl in the 1 position is favored over substitution in the 2 position. As for **1**, the parent neutral compound for **2** or **3**, 1-propen-1-ol, has been observed experimentally[30,35] as a transient species.



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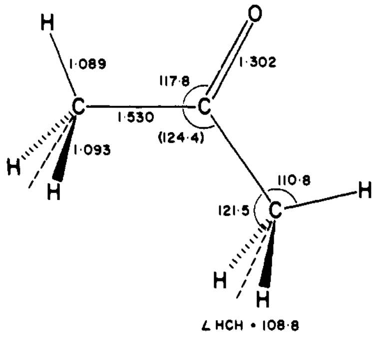
$CH_3C(=O)CH_3^{+\cdot}$ (4). The structure of the 2-propanone (or acetone) radical cation was optimized with C_{2v} symmetry, and the methyl groups were chosen to eclipse the C=O double bond, by analogy with the structure determined for the acetaldehyde radical cation.[16] The electronic state for **4** is $^2A'$, with the odd electron residing in a σ molecular orbital, mainly on oxygen. The relative energy for **4** with respect to its enol isomer **1** is found to be 20 kJ mol^{-1}. This is less than the energy difference of 42 kJ mol^{-1} which was calculated at a similar level of theory for the corresponding $C_2H_4O^{+\cdot}$ isomers,[16] the acetaldehyde and vinyl alcohol radical cations, and shows that a methyl substituent in the 1 position *stabilizes* the keto isomer relative to the enol isomer. Experimentally the heat of formation of **4** is known,[36] and will be used in discussions of other $C_3H_6O^{+\cdot}$ radical cations for which heats of formation are known.



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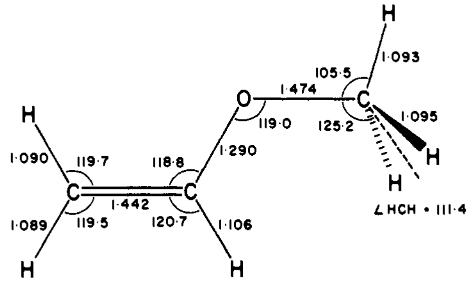
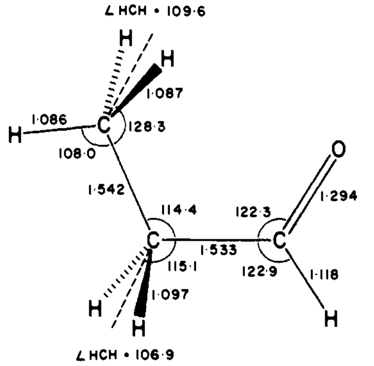
$CH_2{=}CHOCH_3^{+\cdot}$ (5). The starting point for the optimization of the methoxyethene or methyl vinyl ether radical cation (**5**) was the structure of the vinyl alcohol radical cation, with a methyl group substituted for the hydroxylic hydrogen and located anti with respect to the double bond. This geometry was optimized constraining C_s symmetry. An STO-3G optimized structure of the parent molecule, methyl vinyl ether, is available,[37] and a comparison of the geometries shows a substantial shortening of the central C—O bond (1.290 vs. 1.400 Å) and a lengthening of the C=C double bond (1.442 vs. 1.312 Å). This result parallels the effect of ionization for the parent molecule, vinyl alcohol. Isomer **5** has an electron removed from a π-type orbital which is bonding for the C=C double bond, and antibonding for the central C—O bond, consistent with the observed structural changes. The methyl vinyl ether radical cation is quite low in energy, being only 54 kJ mol^{-1} higher in energy than **1**.



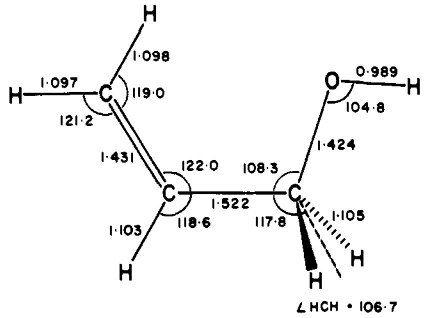
5

$CH_3CH_2CH{=}O^{+\cdot}$ (6). For the optimization of the radical cation of propanal, the structure of the acetaldehyde radical cation[16] with a methyl group substituted on the α carbon and eclipsing the C=O bond was taken as a starting geometry. The optimized structure of **6** (C_s symmetry) resembles closely the acetaldehyde radical cation, and the electronic ground state is the same, the odd electron residing in a σ molecular orbital mainly on the oxygen. The relative energy calculated for the propanal radical cation with respect to the acetone radical cation (**4**) is 73 kJ mol^{-1}, which can be compared with the experimental energy difference of 51 kJ mol^{-1} from thermochemical measurements (Table I). The energy difference between **6** and its enol isomer **2** is calculated to be 80 kJ mol^{-1}, a value which is higher than the keto-enol energy difference of 42 kJ mol^{-1} calculated for the $C_2H_4O^{+\cdot}$ isomers.[16] This implies that an α-methyl substituent destabilizes the acetaldehyde radical cation relative to the vinyl alcohol radical cation, a result similar to that found for α-methyl substitution in the corresponding neutral C_2H_4O isomers.[38,39]



6

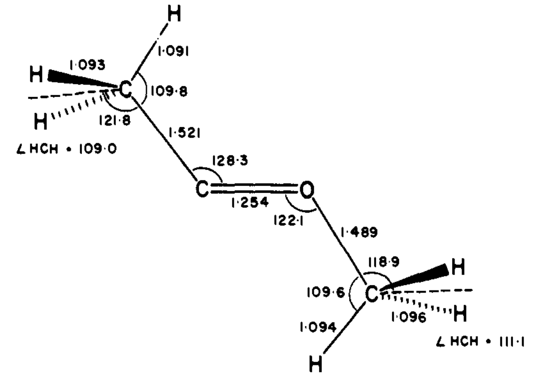
$CH_2{=}CHCH_2OH^{+\cdot}$ (7). The 2-propen-1-ol (or allyl alcohol) radical cation was optimized in the conformation shown, subject to C_s symmetry only. It is interesting to compare the geometry of **7** with the geometries of the closely related isomers



7

1-3. The fact that in 7 the double bond and the hydroxyl group are not adjacent is reflected in the bond lengths concerned. The length of the C=C double bond is similar to the values obtained for **1** and **2** (1.431 vs. 1.454 and 1.430 Å) but the C—O bond length is longer than the corresponding C—O bond lengths in **1** and **2** (1.424 vs. 1.307 and 1.311 Å). In fact, the C-O bond length and the COH angle have not changed significantly upon ionization of **7**; this is seen clearly by comparison with the corresponding STO-3G values for neutral methanol[40] (1.424 vs. 1.433 Å and 104.8 vs. 103.8°, respectively). The electronic structure of **7** is consistent with the calculated geometrical parameters in that an electron has been removed from a π-type orbital which is bonding across the C=C double bond. Unlike the $C_3H_6O^{+\cdot}$ isomers **1-6**, **7** has not yet been established as a stable, identifiable isomer; upon electron impact ionization, the molecular ion of allyl alcohol is believed to isomerize to the enol ion **2**.[11] We have not investigated this rearrangement theoretically.

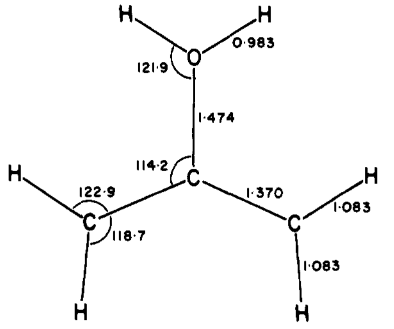
CH_3CO-$CH_3^{+\cdot}$ (8). By analogy with the two carbenoid $C_2H_4O^{+\cdot}$ isomers, the hydroxyethylidene (CH_3COH) and methoxymethylene (CH_3OCH) radical cations, which were found[16] to be relatively low in energy, the methoxyethylidene radical cation (**8**) was also examined. The conformation shown was selected on the basis of the results for the $C_2H_4O^{+\cdot}$ isomers, and optimized constraining C_s symmetry.



8

The central C—O bond is depicted as a double bond, and the calculated bond length substantiates this; it is, for example, shorter than the C=O bonds in **4** and **6** (1.254 vs. 1.302 and 1.294 Å, respectively). The stability of **8** will in part depend on the barrier for the 1,2-hydrogen shift in the ethylidene moiety, which would lead to the more stable isomer **5**. In our study of the $C_2H_4O^{+\cdot}$ isomers,[16] we found such barriers to be substantial, and on the basis of that result we would expect the barrier for a 1,2-hydrogen shift in **8** to be also large. Finally, one should consider the possibility of **8** dissociating into $CH_3C{=}O^+$ and $CH_3^{\cdot}$. The total heat of formation ($\Delta H_f^\circ(298)$) for these fragments[36] is 772 kJ mol^{-1}. Examination of Table I shows that the heat of formation of **8**, estimated from calculated relative energies and known heats of formation for **4**, **6**, **13**, and **15**, is 785-810 kJ mol^{-1}. Thus the dissociation of **8** into $CH_3C{=}O^+$ and $CH_3^{\cdot}$ might be an exothermic process. Finally we note that the electronic structure of **8** is similar to the electronic structures found for the two related $C_2H_4O^{+\cdot}$ isomers, the odd electron residing in a σ orbital.

$CH_2C(OH)_2CH_2^{+\cdot}$ (9). Although this isomer was originally proposed as the product ion from the double McLafferty rearrangement of aliphatic ketones, subsequent experimental studies[2-4] showed that the $C_3H_6O^{+\cdot}$ ion formed in the rearrangement had exclusively the enol ion structure **1**. We have optimized **9**, subject to a C_{2v} symmetry constraint, and find it to be 111 kJ mol^{-1} higher in energy than the enol isomer **1**, which is consistent with the experimental findings.[2-4]



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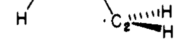
$CH_3CHOCH_2^{+\cdot}$ (10). Previous theoretical[15,16] and experimental[18,19] studies on the ethylene oxide radical cation had supported the existence of a C···C ring-opened isomer which was low in energy and had an asymmetric structure (**18**). We therefore considered the possibility that ion **10**, which formally could arise by C···C ring opening of ionized propylene oxide (**15**), could be a stable observable $C_3H_6O^{+\cdot}$ species. A preliminary calculation involving the substitution of a methyl group in **18** at C_1 or C_2 showed a preference for substitution on the planar carbon (i.e., C_1). Optimization of this geometry (C_s symmetry) resulted in **10**, which has a quite low relative energy, being 112 kJ mol^{-1} higher than **1**.



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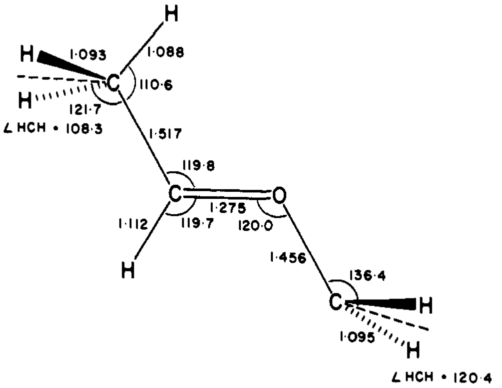
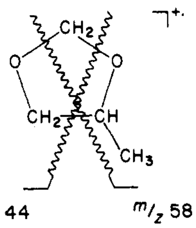


10

Like the $C_2H_4O^{+\cdot}$ isomer (**18**), **10** has an odd electron in a σ-type molecular orbital and has one C-O bond considerably longer than the other. This suggests that, if ion **10** exists, it should react via a $CH_2^{+\cdot}$ transfer. Our ICR experiments have shown that the m/z 58 ion from 4-methyl-1,3-dioxolane (**19**), which is assumed to arise via loss of formaldehyde as shown, transfers $CH_2^{+\cdot}$ to acetonitrile, as also does the m/z 44 ion which is formed by the alternative breakdown pathway. This

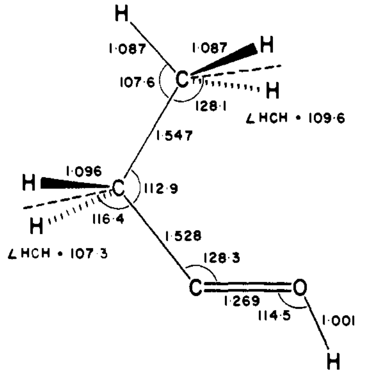


19

latter ion can be considered to have the structure **18** by analogy with our ICR studies on the $C_2H_4O^{+\cdot}$ ion from 1,3-dioxolane.[19]

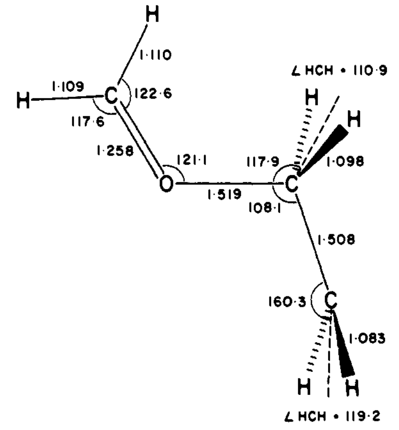
On the other hand, the molecular ion of propylene oxide does *not* exhibit any measurable $CH_2^{+\cdot}$ transfer to acetonitrile or any other suitable neutral. We interpret these results to mean that some or all of the m/z 58 ion from **19** has structure **10** while, unlike the ethylene oxide ion,[19] ionized propylene oxide retains its cyclic structure **15.** Even though our calculations show that **10** is lower in energy than **15** by 95 kJ mol^{-1}, C···C ring opening may not occur to give the more stable isomer **10** if there is a high energy barrier to the isomerization of **15** to **10** or if alternative breakdown pathways are energetically more favorable.

$CH_3CH_2COH^{+\cdot}$ (11). As the hydroxypropylidene radical cation (**11**) is closely related to its $C_2H_4O^{+\cdot}$ homologue, optimization was started from the geometry of the hydroxyethylidene radical cation ($CH_3COH^{+\cdot}$), with a methyl substituent added (C_s symmetry). The resulting structure is very similar to its lower homologue, and is 123 kJ mol^{-1} higher than **1.** The electronic state of **11** is the same as for **8** ($^2A'$). Isomerization of **11** to **2**, **3**, or **6** by way of a 1,2-hydrogen shift has been studied for similar situations in the $CH_2O^{+\cdot}$ and $C_2H_4O^{+\cdot}$ systems[16,17] and is unlikely. Dissociation of **11** to give $CH_3CH_2C{=}O^+$ and H· should be considered in order to assess its stability. The combined heat of formation[36] of $CH_3CH_2C{=}O^+$ and H· is 820 kJ mol^{-1}, a value marginally higher than the heat of formation of **11** (795–820 kJ mol^{-1}) estimated from Table I. Thus **11,** although higher in energy than **8,** has a better chance of being observed because of the absence of an exothermic dissociative pathway.



11

$CH_2{=}OCH_2CH_2^{+\cdot}$ (12). This isomer, which formally is a C···C ring-opened isomer of the trimethylene oxide radical cation (**13**), was optimized in the conformation shown, constraining C_s symmetry, and is found to be 10 kJ mol^{-1} lower in energy than **13.** The most interesting feature of **12** is that it can be considered to be a higher homologue of the C···C ring-opened ethylene oxide ion (**18**). Whereas for **18** ICR experiments show a $CH_2^{+\cdot}$ transfer to occur to suitable substrates such as nitriles,[19] **12** might be expected to show $C_2H_4^{+\cdot}$ transfer to a suitable substrate. A reaction of this type can be related to a recently reported[41] ion/molecule reaction in which $CH_3O^+HCH_2CH_2\cdot$ transfers a $C_2H_4^{+\cdot}$ moiety to various nitriles. In all cases the driving force could be considered to be the loss of a small, stable fragment, namely, CH_2O or CH_3OH.



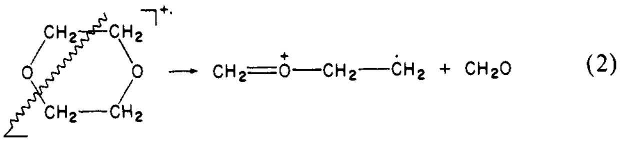
12

When a mixture of trimethylene oxide and acetonitrile was examined in the ICR spectrometer, a weak but observable $C_2H_4^{+\cdot}$ transfer reaction from the m/z 58 ion of trimethylene oxide to acetonitrile was observed, which we believe could proceed via reaction 1.

$$\mathbf{13} \rightarrow \underset{\mathbf{12},\ m/z\ 48}{CH_2{=}\overset{+}{O}CH_2\dot{C}H_2} + CH_3CN$$

$$\rightarrow \underset{m/z\ 69}{CH_3CNC_2H_4^{+\cdot}} + CH_2O \quad (1)$$

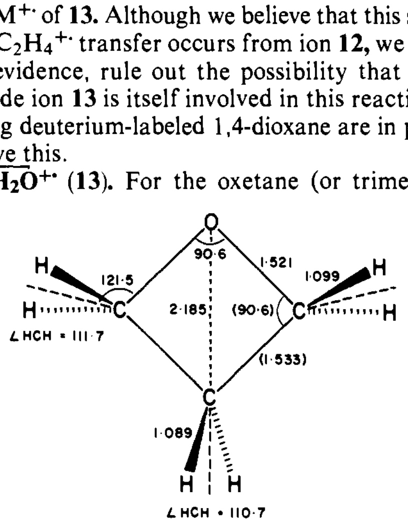
As a possible alternative precursor of the $C_3H_6O^{+\cdot}$ isomer **12,** we chose to look at 1,4-dioxane (**20**), which has a prominent fragment ion at m/z 58 in its mass spectrum. This arises by loss of CH_2O from $M^{+\cdot}$ and could have structure **12** (cf. reaction 2).



20, m/z 88 12, m/z 58

In the ICR spectrometer, the m/z 58 ion from 1,4-dioxane shows a much more efficient transfer of $C_2H_4^{+\cdot}$ to acetonitrile than does the $M^{+\cdot}$ of **13.** Although we believe that this strongly suggests that $C_2H_4^{+\cdot}$ transfer occurs from ion **12,** we cannot, on available evidence, rule out the possibility that the trimethylene oxide ion **13** is itself involved in this reaction. Experiments using deuterium-labeled 1,4-dioxane are in progress to try to resolve this.

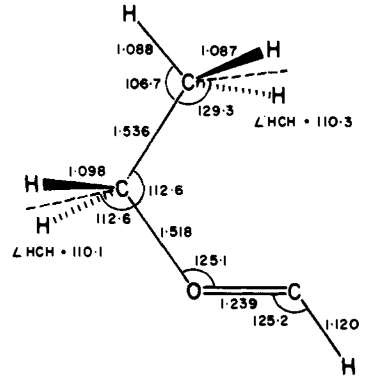
$\overline{CH_2CH_2CH_2O}^{+\cdot}$ (13). For the oxetane (or trimethylene oxide) radical cation, C_s distorted structures were allowed in the optimization process, but the fully optimized structure has C_{2v} symmetry. As noted above, however, STO-3G fails to re-



13

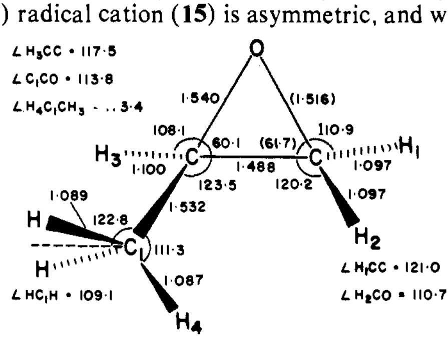
produce the slight ring puckering of cyclobutane.[26] The odd electron resides in a π-type orbital centered mainly on oxygen, and **13** has the same electronic state as the ethylene oxide radical cation ($^2B_1$). Experimentally neutral oxetane is found to have an essentially planar heavy-atom skeleton, although the microwave spectrum suggests that a small amount of ring puckering occurs.[42] Since the heat of formation of **13** is known, the calculated energy differences between **13** and **4** and **6** can be compared with the experimental values. The theoretical values of 137 and 64 kJ mol^{-1}, respectively, compare reasonably well with the experimental values of 133 and 82 kJ mol^{-1}.

$CH_3CH_2OCH^{+\cdot}$ (14). The ethoxymethylene radical cation (**14**) is closely related to its $C_2H_4O^{+\cdot}$ homologue, the methoxymethylene radical cation ($CH_3OCH^{+\cdot}$), the structure of which was substituted with a methyl group, and fully optimized with C_s symmetry. The electronic ground state of **14**, as for **8** and **11**, is $^2A'$. The stability of **14** with respect to dissociation into $CH_3CH_2O{=}C^+$ and H· cannot be assessed in the same manner as for **8** and **12**, since no experimental heat of formation is available for $CH_3CH_2O{=}C^+$. We do know, however, that $HO{=}C^+$ is 91 kJ mol^{-1} (4-31G//4-31G)[43] higher in energy than $HC{=}O^+$. If we take this as an estimate for the energy difference between $CH_3CH_2O{=}C^+$ and $CH_3CH_2C{=}O^+$, we obtain a total heat of formation of about 910 kJ mol^{-1} for $CH_3CH_2O{=}C^+$ and H·. For an alternative dissociation into $CH_3CH_2\cdot + HCO^+$, we obtain[36] a total heat of formation of 923 kJ mol^{-1}. Thus, either of these dissociations is likely to be an endothermic process. We have not examined other possible dissociation pathways for **14**.



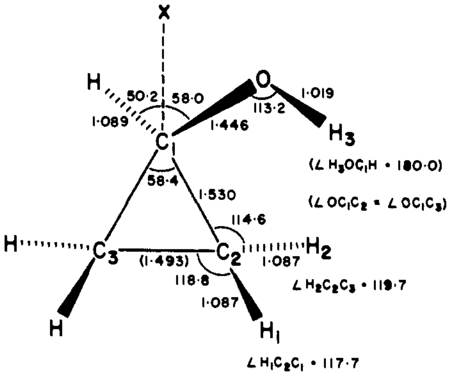
14

$CH_3\overline{CHCH_2O}^{+\cdot}$ (15). The methyloxirane (or propylene oxide) radical cation (**15**) is asymmetric, and was optimized as such constraining local C_s symmetry for the methyl group only. Experimentally **15** is known as a stable isomer, and its heat of formation is available. Comparison of the energy of **15** relative to the energies of **4**, **6**, and **13** for which $\Delta H_f°(298)$ values are also available shows good agreement between theory and experiment (186, 114, and 49 vs. 174, 123, and 41 kJ mol^{-1}, respectively).



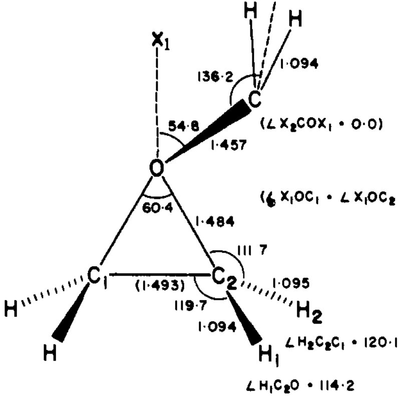
15

$\overline{CH_2CH_2CH}OH^{+\cdot}$ (16). We examined the cyclopropanol radical cation in the conformation with C_s symmetry as shown. It is found that an electron has been removed from a molecular orbital with A″ symmetry, and the odd electron is located mainly on oxygen, which results in a large COH angle, as was found for the COH angles in **1** and **2**. Experimentally **16** has been studied,[14] but not as yet uniquely characterized as an identifiable $C_3H_6O^{+\cdot}$ isomer, nor is any experimental information available on its $\Delta H_f°$ value.



16

$\overline{CH_2CH_2O}CH_2^{+\cdot}$ (17). This isomer is of special interest since it has been proposed[18] as an intermediate in the reaction of the C···C ring-opened ethylene oxide ion (**18**) with ethylene oxide, in which the ion **18** transfers a $CH_2^{+\cdot}$ moiety to the neutral ethylene oxide molecule. The proposed reaction mechanism based on deuterium-labeling experiments includes a rearrangement of the intermediate (**17**) to the trimethylene oxide ion (**13**), which subsequently has to lose a hydrogen radical to explain a product of *m/z* 57.



17

Initially optimization of **17** indicated that the CH_2 moiety preferred to be out of the plane of the ring, in an anti arrangement with respect to the ring about the C-O bond giving rise to a structure with C_s symmetry. This structure was fully optimized, and the odd electron is found to be centered on the free methylene group. The total energy of **17** is quite high, but not substantially higher than the known $C_3H_6O^{+\cdot}$ isomers **15** and **16**. The energy changes for the reaction scheme proposed by Beauchamp et al. can be obtained using 4-31G//STO-3G total energies[44] and confirm the exothermicity of the more important steps. The initial step is found to be exothermic by 71 kJ mol^{-1}, and the subsequent rearrangement **17** → **13** is exothermic by 89 kJ mol^{-1}. The rearrangement of **17** to **12** is even more exothermic but deuterium-labeling experiments[18] require the intermediacy of the cyclic structure **13**.

Conclusions

The study of the $C_3H_6O^{+\cdot}$ radical cations described here has resulted in the ranking of known, and as yet unknown, $C_3H_6O^{+\cdot}$ isomers according to their relative energies. For those isomers for which experimental heats of formation are available, a reasonable agreement with the theoretical results is found. Consistent with theoretical and experimental results for the $C_2H_4O^{+\cdot}$ isomers, we find that the enol isomers $CH_2{=}C(OH)CH_3^{+\cdot}$ (**1**) and $CH_3CH{=}CHOH^{+\cdot}$ (**2** and **3**) are the lowest energy $C_3H_6O^{+\cdot}$ isomers. The three carbenoid radical cations **8**, **11**, and **14** that have been examined are relatively low in energy, and might be observable $C_3H_6O^{+\cdot}$ isomers, depending on their stability with respect to dissociation. Two of the $C_3H_6O^{+\cdot}$ isomers that have been examined correspond to C···C ring-opened propylene oxide (**10**) and C···C ring-opened trimethylene oxide (**12**) and are found to be relatively low in energy. ICR experimental results are reported which are consistent with our calculations on the stabilities and structures of these two ions. Our theoretical study has shown a total of 15 isomers of $C_3H_6O^{+\cdot}$ that have an energy less than or equal to that of the experimentally characterized propylene oxide cation.[46]

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(44) The 4-31G//STO-3G energy for $\underline{CH_2{=}O^+CH_2}$ = −152.321 24,[16] for $CH_2{=}O$ = −113.691 71,[40] for $\overline{CH_2CH_2O}$ = −152.624 44[45] hartrees.
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(46) NOTE ADDED IN PROOF. Since submission of this manuscript, additional unpublished experimental data for some of the $C_3H_6O^{+\cdot}$ isomers have been brought to our attention.[47] These include $\Delta H_f°(298°)$ values of 661 kJ mol^{-1} for **1**, 665 kJ mol^{-1} for **2**, 741 kJ mol^{-1} for **5**, and 799 kJ mol^{-1} for **7**. The ordering of these and the other experimental values shown in Table I is in complete agreement with our theoretical results. However, the experimental data for the enols **1** and **2** suggest that their relative energies appear to be somewhat overestimated in our theoretical treatment. Calculations designed to examine this discrepancy are in progress.
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