

The Potential Energy Surface for the $[\text{C}_2\text{H}_2\text{O}]^{++}$ System: The Ketene Radical Cation $[\text{CH}_2=\text{C}=\text{O}]^{++}$ and its Isomers

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Ab initio molecular orbital calculations with large, polarization basis sets and incorporating valence electron correlation have been employed to examine the $[\text{C}_2\text{H}_2\text{O}]^{++}$ potential energy surface. Four $[\text{C}_2\text{H}_2\text{O}]^{++}$ isomers have been identified as potentially stable, observable ions. These are the experimentally well-known ketene radical cation, $[\text{CH}_2=\text{C}=\text{O}]^{++}$ (a), and the presently unknown ethynol radical cation, $[\text{CH}\equiv\text{C}-\text{OH}]^{++}$ (b), the oxirene radical cation $[\text{CH}=\text{CH}-\text{O}]^{++}$ (c) and an ion resembling a complex of CO with $[\text{CH}_2]^{++}$, $[\text{:C}=\text{O}-\text{CH}_2]^{++}$ (d). The calculated energies of b, c and d relative to a are 189, 257 and 259 kJ mol⁻¹, respectively. Dissociation of ions a and d is found to occur without reverse activation energy.

INTRODUCTION

Although recent advances in experimental techniques have greatly facilitated the study of the thermochemistry and molecular structure of gas phase ions, this is still an area where there are often problems in unambiguously interpreting the experimental results. In this respect, theoretical calculations of ion structure and stability are playing an increasingly valuable role in assisting, and at times guiding, experimental research.

We have used such a theoretical approach in this paper to examine the $[\text{C}_2\text{H}_2\text{O}]^{++}$ system, for which relatively little is known experimentally. The neutral $\text{C}_2\text{H}_2\text{O}$ system has been the subject of numerous experimental and theoretical studies¹⁻³ aimed at determining whether, in addition to ketene ($\text{CH}_2=\text{C}=\text{O}$), there may exist other stable $\text{C}_2\text{H}_2\text{O}$ isomers. Calculations have identified¹ ethynol ($\text{CH}\equiv\text{C}-\text{H}$) and oxiranylidene ($\text{CH}_2-\text{O}-\text{C:}$) as potentially observable species. For the ionized system, the ketene radical cation, $[\text{CH}_2=\text{C}=\text{O}]^{++}$, is the only $[\text{C}_2\text{H}_2\text{O}]^{++}$ isomer whose observation has been reported to date. The ionization of ketene, leading to $[\text{CH}_2=\text{C}=\text{O}]^{++}$, has been studied extensively.⁴⁻¹⁰ In addition, ions of composition $[\text{C}_2\text{H}_2\text{O}]^{++}$ have been observed in the mass spectra of aliphatic esters,¹¹ furan¹²⁻¹⁴ and cyclobutanone,¹⁵ and have generally been assumed to have the ketene structure. Photoionization, photoelectron spectroscopy and mass spectrometry studies of the ionization and fragmentation of ketene to give $[\text{CH}_2]^{++}$ and CO have been carried out,¹⁶⁻¹⁸ and ion/molecule reactions of the ketene radical cation^{9,19} as well as ion/molecule reactions leading to the ketene radical cation²⁰ have been reported. We are not aware of any reports of $[\text{C}_2\text{H}_2\text{O}]^{++}$ isomers other than the ketene radical cation, nor of any attempts at generating such isomers.

In the present study, we aim to examine the $[\text{C}_2\text{H}_2\text{O}]^{++}$ potential energy surface, and to determine

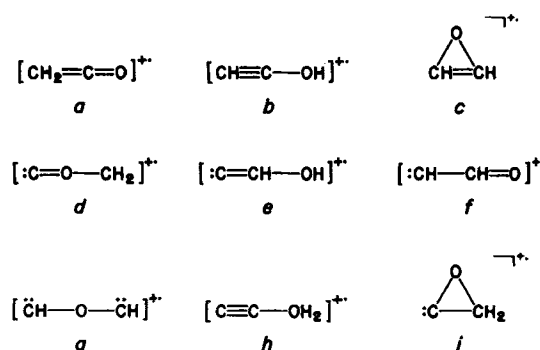


Figure 1. Possible isomeric $[\text{C}_2\text{H}_2\text{O}]^{++}$ structures.

which $[\text{C}_2\text{H}_2\text{O}]^{++}$ isomers, if any, are likely to be stable, observable species. For this purpose, we have considered nine possible $[\text{C}_2\text{H}_2\text{O}]^{++}$ isomers (a-i, Fig. 1) and a number of transition structures for their interconversion. The latter will enable us to assess the stability of the $[\text{C}_2\text{H}_2\text{O}]^{++}$ isomers under scrutiny. We are not aware of any previous theoretical studies of the $[\text{C}_2\text{H}_2\text{O}]^{++}$ system other than a discussion²¹ of the dissociation of $[\text{CH}_2=\text{C}=\text{O}]^{++}$ (a) to give $[\text{CH}_2]^{++}$ and CO, and a MINDO/3 study²² of a.

METHOD AND RESULTS

Ab initio molecular orbital calculations were performed with a modified version²³ of the Gaussian 80 system of programs.²⁴ Geometries of equilibrium structures and transition structures were determined at the Hartree-Fock (HF) level using analytical gradient procedures and the 3-21G basis set.²⁵ Improved relative energies were obtained from higher level calculations which employ the d- and dp-polarization 6-31G* and 6-31G** basis sets²⁶ and which incorporate valence electron correlation via second-order (MP2) and third-order (MP3) Møller-Plesset perturbation

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theory.²⁷ All calculations on odd-electron species employ the spin-unrestricted formalism. As computational expense precluded direct calculation of MP3/6-31G** energies, these were estimated using the additivity relationship:

$$\begin{aligned}\Delta E(\text{MP3/6-31G}^{**}) &\approx \Delta E(\text{MP3/6-31G}^*) \\ &+ \Delta E(\text{MP2/6-31G}^{**}) \\ &- \Delta E(\text{MP2/6-31G}^*) \quad (1)\end{aligned}$$

Such additivity relationships have recently been tested and found to hold well.²⁸

Optimized structures were confirmed as minima (equilibrium structures) or saddle points (transition structures) by evaluation of the full set of harmonic

vibrational frequencies²⁹ at the HF/3-21G level. In addition, the calculated frequencies were used to obtain zero-point vibrational energies. Energy comparisons refer to MP3/6-31G** values with the addition of a contribution for zero-point vibrations. As HF/3-21G calculations are known to overestimate vibrational frequencies by ~10%,³⁰ the zero-point vibrational energy contributions have been scaled by a factor of 0.9.

Optimized geometries of $[\text{C}_2\text{H}_2\text{O}]^{++}$ equilibrium structures and transition structures are displayed within the text; bond lengths are given in Ångströms, bond angles in degrees. The optimized geometries of the corresponding neutral $\text{C}_2\text{H}_2\text{O}$ equilibrium structures (distinguished by a parenthetic (*n*)) are provided

Table 1. Calculated total energies (Hartrees^a) and zero-point vibrational energies (ZPVE, kJ mol⁻¹) for the $[\text{C}_2\text{H}_2\text{O}]^{++}$ and component systems^b

Species	Symmetry	Electronic state	3-21G	6-31G*	6-31G**	MP2/6-31G*	MP2/6-31G**	MP3/6-31G*	ZPVE ^c
$[\text{CH}_2=\text{C}=\text{O}]^{++}$ (a)	C_{2v}	$^2\text{B}_1$	-150.56921	-151.42379	-151.42776	-151.81216	-151.82650	-151.81853	87.3
$[\text{CH}\equiv\text{C}-\text{OH}]^{++}$ (b)	C_s	$^2\text{A}''$	-150.49920	-151.34377	-151.35296	-151.72856	-151.74610	-151.74299	86.1
$[\text{CH}=\text{CH}-\text{O}]^{++}$ (c1)	C_{2v}	$^2\text{B}_1$	-150.44604	-151.30882	-151.31317	-151.70859	-151.72233	-151.72034	85.2 ^d
$[\text{CH}=\text{CH}-\text{O}]^{++}$ (c2)	C_s	$^2\text{A}''$	-150.44637	-151.30837	-151.31275	-151.70186	-151.71559	-151.71472	80.5
$[:\text{C}=\text{O}-\text{CH}_2]^{++}$ (d)	C_s	$^2\text{A}'$	-150.49923	-151.33794	-151.34189	-151.70422	-151.71898	-151.71689	79.6
$[:\text{C}=\text{CH}-\text{OH}]^{++}$ (e1)	C_s	$^2\text{A}''$	-150.42752	-151.28603	-151.29488	-151.64814	-151.66622	-151.67078	°
$[:\text{C}=\text{CH}-\text{OH}]^{++}$ (e2)	C_s	$^2\text{A}''$	-150.42371	-151.28263	-151.29145	-151.64563	-151.66364	-151.66781	85.1 ^f
$[:\text{C}-\text{CH}=\text{O}]^{++}$ (f)	C_s	$^2\text{A}''$	-150.44668	-151.29265	-151.29698	-151.62986	-151.64390	-151.65604	77.7
TS(f → a) (j)	C_s	$^2\text{A}''$	-150.43529	-151.28842	-151.29469	-151.64989	-151.66582	-151.67075	68.1
TS(f → b) (k)	C_s	$^2\text{A}''$	-150.37348	-151.22118	-151.22917	-151.59405	-151.61122	-151.60944	62.7
TS(f → c) (l)	C_s	$^2\text{A}''$	-150.44525	-151.29741	-151.30180	-151.66245	-151.67632	-151.68136	76.7 ^a
TS(d → a) (m)	C_s	$^2\text{A}'$	-150.44352	-151.30559	-151.30993	-151.66754	-151.68183	-151.67809	68.6 ^a
TS(e → b) (n)	C_s	$^2\text{A}''$	-150.37561	-151.24104	-151.25384	-151.63192	-151.65323	-151.64749	65.0
$\text{C}\equiv\text{O}$	$\text{C}_{\infty v}$	$^1\text{A}_1$	-112.09330	-112.73726	-112.73726	-113.02014	-113.02014	-113.01837	13.8
$[\text{CH}_2]^{++}$	C_{2v}	$^2\text{A}_1$	-38.34747	-38.56612	-38.57055	-38.63519	-38.64929	-38.64940	45.0

^a 1 Hartree = 2625.5 kJ mol⁻¹.

^b Optimized at the HF/3-21G level.

^c 3-21G//3-21G values unless otherwise stated.

^d 6-31G**//6-31G* value.

^e Not obtained, due to convergence problems.

^f Obtained with a convergence criterion of 10⁻⁶ Hartrees, rather than 10⁻⁷ Hartrees, due to convergence problems.

^g The zero-point vibrational energy calculations indicate a small additional imaginary frequency, which has been ignored.

Table 2. Calculated relative energies (kJ mol⁻¹) for the $[\text{C}_2\text{H}_2\text{O}]^{++}$ system

Species	3-21G	6-31G*	6-31G**	MP2/6-31G*	MP2/6-31G**	MP3/6-31G*	MP3/6-31G***	MP3/6-31G*** ^b
$[\text{CH}_2=\text{C}=\text{O}]^{++}$ (a)	0	0	0	0	0	0	0	0
$[\text{CH}\equiv\text{C}-\text{OH}]^{++}$ (b)	184	210	196	219	211	198	190	189
$[\text{CH}=\text{CH}-\text{O}]^{++}$ (c1)	323	302	301	272	273	258	259	257
$[\text{CH}=\text{CH}-\text{O}]^{++}$ (c2)	323	303	302	290	291	273	274	268
$[:\text{C}=\text{O}-\text{CH}_2]^{++}$ (d)	184	225	225	283	282	267	266	259
$[:\text{C}=\text{CH}-\text{OH}]^{++}$ (e1)	372	362	349	431	421	388	378	376 ^c
$[:\text{C}=\text{CH}-\text{OH}]^{++}$ (e2)	382	371	358	437	428	396	387	385
$[:\text{CH}-\text{CH}=\text{O}]^{++}$ (f)	322	344	343	479	479	427	427	418
TS(f → a) (j)	352	355	349	426	422	388	384	367
TS(f → b) (k)	514	532	521	573	565	549	541	519
TS(f → c) (l)	325	332	331	393	394	360	361	351
TS(d → a) (m)	330	310	309	380	380	369	369	352
TS(e → b) (n)	508	480	457	473	455	449	431	411
$[\text{CH}_2]^{++} + \text{C}\equiv\text{O}$	337	316	315	412	412	396	396	370 ^d

^a Values estimated using Eqn (1).

^b With zero-point energy contribution (see text).

^c Using the ZPVE obtained for e2.

^d The experimental value is 399 kJ mol⁻¹ (see text).

Table 3. Calculated vibrational frequencies^a for equilibrium structures *a-d*

Species	Vibrational frequencies (cm ⁻¹)				
[CH ₂ =C=O] ⁺⁺ (<i>a</i>)	460(b ₂)	509(b ₁)	759(b ₁)	950(a ₁)	1078(b ₂)
	1375(a ₁)	2011(a ₁)	2938(a ₁)	3052(b ₂)	
[CH≡C-OH] ⁺⁺ (<i>b</i>)	457(a')	479(a'')	615(a'')	724(a')	1060(a')
	1143(a')	2066(a')	3165(a')	3224(a')	
[CH=CH-O] ⁺⁺ (<i>c1</i>) ^b	178(b ₂)	741(b ₁)	807(a ₂)	946(a ₁)	1027(b ₂)
	1136(a ₁)	1695(a ₁)	3103(b ₂)	3182(a ₁)	
[CH=O-CH ₂] ⁺⁺ (<i>d</i>)	197(a'')	219(a')	456(a')	731(a')	1047(a'')
	1292(a')	1875(a')	2976(a')	3177(a'')	

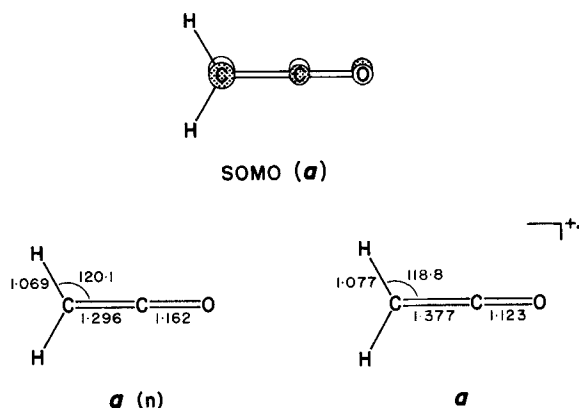
^a Values listed have been scaled by 0.9 (see text).^b Calculated at the 6-31G*/6-31G* level.

for comparison, as well as a schematic representation of the singly occupied molecular orbital (SOMO) of each of the ions. Total energies and zero-point vibrational energies are listed in Table 1, relative energies in Table 2 and harmonic vibrational frequencies for ions *a-d* in Table 3. The more important aspects of the [C₂H₂O]⁺⁺ potential energy surface are illustrated in Figs 2-5. Unless otherwise noted, relative energies quoted within the text refer to our best calculated values from Table 3, i.e. MP3/6-31G** with zero-point energy contribution. Energies calculated at this level have been found to provide a reasonable description of the potential energy surfaces for related systems.³¹

DISCUSSION

Structures and relative energies

The only known [C₂H₂O]⁺⁺ isomer, the ketene radical cation (*a*), is found to have a ²B₁ ground state, and to be the global minimum on the [C₂H₂O]⁺⁺ potential energy surface. Its structure reflects the nature of the SOMO: removal of an electron from a π -type molecular orbital which is bonding across C=C and antibonding across C=O leads to a lengthening of the C=C bond and a shortening of the C=O bond from 1.296 and 1.162 to 1.377 and 1.123 Å, respectively. Vertical (IE_v) and adiabatic (IE_a) ionization energies for ketene were calculated at the MP3/6-31G** level (Table 4) yielding values of 9.44 (IE_v) and 9.09 (IE_a) eV compared with experimental values of 9.8 (IE_v)⁸ and 9.6 (IE_a) eV.^{4-6,8-10} The calculated

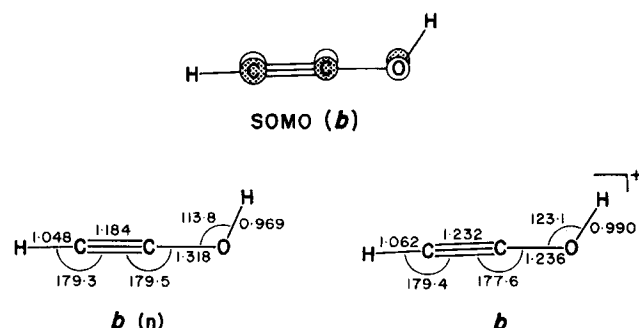
**Table 4. Calculated total energies (Hartrees^a) and ionization energies (IE_v, IE_a, ΔIE, eV) for ketene**

	<i>a</i> (n)	[<i>a</i> (n)] ^{++b}	IE _v	IE _a ^c	ΔIE ^d
6-31G*	-151.72393	-151.41000	8.54	8.17	0.37
6-31G**	-151.72800	-151.41404	8.54	8.17	0.37
MP2/6-31G*	-152.14590	-151.79825	9.46	9.08	0.38
MP2/6-31G**	-152.16189	-151.81264	9.50	9.13	0.37
MP3/6-31G*	-152.15090	-151.80559	9.40	9.04	0.36
MP3/6-31G** ^e	—	—	9.44	9.09	0.35

^a 1 Hartree = 27.212 eV.^b Calculated at the optimized geometry of neutral ketene (*a* (n)).^c Calculated using total energies for *a* listed in Table 1.^d ΔIE = IE_v - IE_a.^e Values estimated using Eqn (1).

difference (ΔIE) of 0.35 eV between IE_a and IE_v reflects the geometric reorganization of ketene upon ionization.

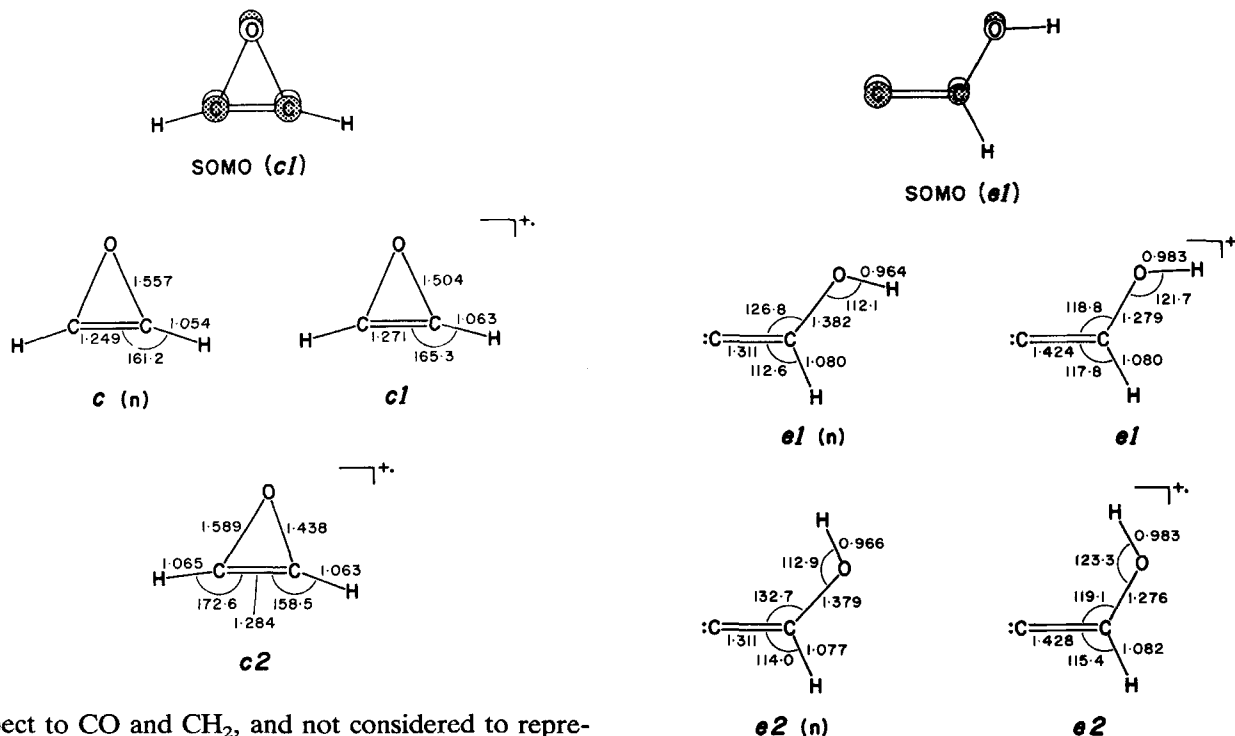
The second lowest isomer, the ethynol radical cation (*b*), is calculated to lie 189 kJ mol⁻¹ higher in energy



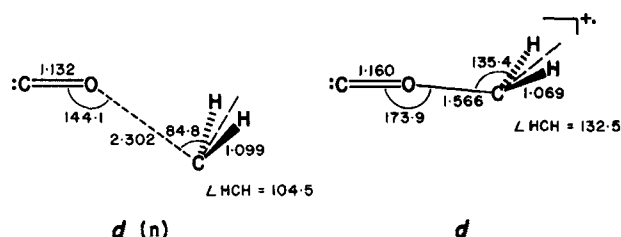
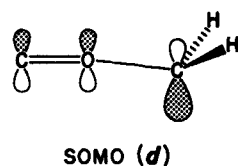
than *a*. This may be compared with an energy difference of 152 kJ mol⁻¹ for the neutral isomers.¹ It is interesting that whereas the ethynol-ketene energy difference has increased (from 152 to 189 kJ mol⁻¹) on ionization, the ethenol (vinyl alcohol)-acetaldehyde energy difference moves in the opposite direction, from 45 to -64 kJ mol⁻¹, on ionization.^{32,33} Ionization in ethynol occurs from a π -type orbital which results in a ²A'' electronic state. The change in structure upon ionization may again be understood by examining the SOMO. The main features are a lengthening of the C≡C bond and a reduction in the C-O bond.

For the oxirene radical cation (*c*), our 3-21G calculations indicate a minimum corresponding to an ion slightly distorted from C_{2v} symmetry (*c2*), the C_{2v} species (*c1*) being slightly higher in energy. Higher level calculations (Table 1) show, however, that the symmetric structure (*c1*) is preferred and this is supported by 6-31G* vibrational frequencies (Table 3) which indicate that *c1* is a local minimum on the potential surface. The energy of *c1* relative to *a* is calculated to be 257 kJ mol⁻¹, substantially lower than the value of 331 kJ mol⁻¹ which was obtained for the relative energies of the corresponding neutral isomers.¹ Structural changes upon ionization again are consistent with the nature of the SOMO, viz. a lengthening of the C=C bond and a reduction in the C-O bond lengths.

For the neutral C₂H₂O system, the C≡O-CH₂ isomer was found¹ to be only weakly bound with



respect to CO and CH_2 , and not considered to represent a viable $\text{C}_2\text{H}_2\text{O}$ species. However, ionization to give $[\text{:C=O-CH}_2]^{++}(\text{d})$ results in a substantial stabilization. The energy of *d* relative to *a* is calculated to be 259 kJ mol^{-1} . Ion *d* is bound with respect to CO and $[\text{CH}_2]^{++}$ by 111 kJ mol^{-1} ; this is reflected in the calculated structure of *d*, where the C—O bond length is 1.566 \AA compared with 2.302 \AA in the weak, neutral $\text{C}\equiv\text{O}\cdots\text{CH}_2$ complex.

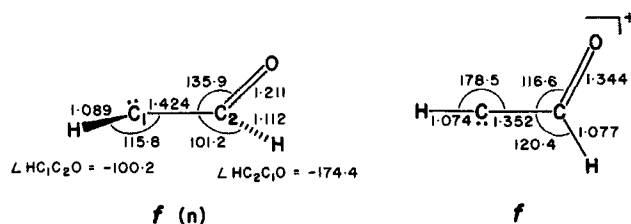
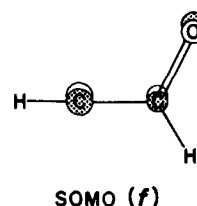


The $[\text{CH}_2=\text{C=O}]^{++}/[\text{:C=O-CH}_2]^{++}$ pair of isomers may be compared with the related $[\text{H-C}\equiv\text{O}]^{++}/[\text{:C=O-H}]^{++}$ and $[\text{CH}_3-\text{C}\equiv\text{O}]^{++}/[\text{:C=O-CH}_3]^{++}$ ion systems.^{34,35} For the latter systems, energy differences of 157 and 216 kJ mol^{-1} , respectively, were calculated. The common feature of these three isomer pairs is the attachment of a small group ($[\text{CH}_2]^{++}$, $[\text{H}]^{++}$, $[\text{CH}_3]^{++}$) to either end of a carbon monoxide moiety. Attachment to the carbon end is favoured in each case. We note that the higher energy isomer of $[\text{HCO}]^{++}$, viz. $[\text{COH}]^{++}$, has recently been identified experimentally.³⁶

The hydroxyvinylidene radical cation, $[\text{:C=CH-OH}]^{++}$, was studied in both *anti* and *syn* conformations. The *anti* conformer (*e1*) was calculated to be

the lower in energy, but still 376 kJ mol^{-1} higher in energy than *a*. Again the nature of the SOMO allows a rationalization of the structural changes upon ionization: the increase in the C=C bond length may be attributed to the removal of an electron from a molecular orbital which is bonding in the C=C region.

The formylmethylene molecule (:CH-CH=O) has often been invoked as an intermediate in the Wolff rearrangement. Recent calculations,¹ however, suggest that formylmethylene is not stable but will rearrange to ketene without activation energy. The formylmethylene radical cation (*f*) is also likely to be unsta-



ble with respect to rearrangement to the ketene radical cation (*a*) (see below). However, it is located at a minimum on the 3-21G surface where it is found to be planar, in contrast to the non-planar structure found for the neutral species. The energy of *f* relative to the ketene radical cation (*a*) is quite high at 418 kJ mol^{-1} .

For the remaining $[\text{C}_2\text{H}_2\text{O}]^{++}$ isomers (*g-i*) considered in this study, initial calculations showed *g* and *h*

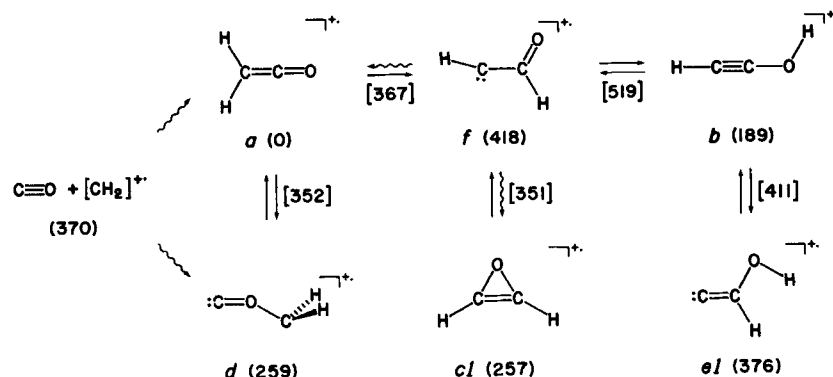


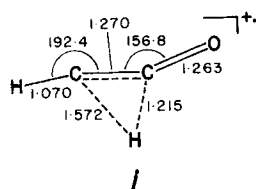
Figure 2. Interconversion pathways between $[\text{C}_2\text{H}_2\text{O}]^+$ isomers. Relative energies shown in parentheses are for equilibrium structures; those in square brackets are for transition structures. Curly arrows indicate a barrier-free process.

to be very high in energy relative to the most stable species (*a*), while ion *i*, the oxiranylidene radical cation, was found to collapse to *a* without a barrier. The latter result contrasts with that found for oxiranylidene itself, which was indicated to be a potentially observable $\text{C}_2\text{H}_2\text{O}$ species.¹

Intramolecular rearrangement pathways

For a $[\text{C}_2\text{H}_2\text{O}]^+$ isomer other than the ketene radical cation (*a*) to be a stable, observable species, it must be of low relative energy and must have substantial barriers with respect to rearrangement to *a* or any other isomer with an energy lower than the ion under consideration. For this reason, we have determined the potential energy barriers for a number of rearrangements involving ions *a*–*f*, as given by the relative energies of the transition structures for such rearrangements. A summary of our results for various possible intramolecular and dissociative rearrangements of ions *a*–*f* is presented in Fig. 2.

At the 3-21G level, a transition structure (*j*) was



found for the rearrangement of the formylmethylene radical cation (*f*) to the ketene radical cation (*a*) by way of a 1,2-hydrogen shift. The associated barrier is calculated to be 30 kJ mol^{-1} , but higher level calculations show that the energy of *j* drops below that of *f* (Tables 1 and 2), suggesting that *f*, if formed, is likely to rearrange to *a* without activation energy. Thus, *f* is unlikely to represent a stable structure on the $[\text{C}_2\text{H}_2\text{O}]^+$ potential energy surface.

Transition structure *k* represents the barrier for the

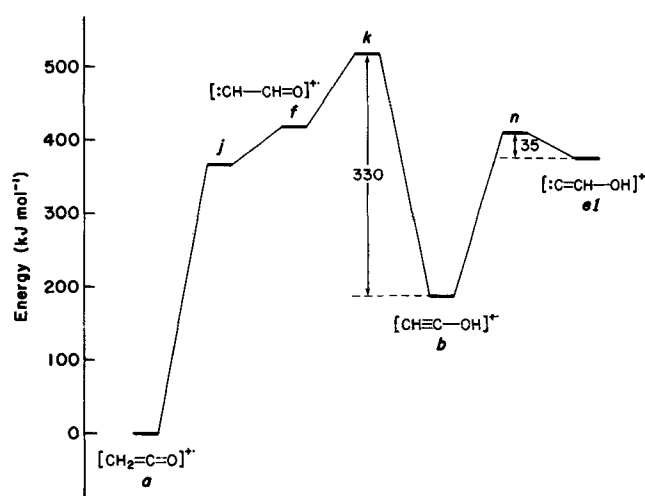
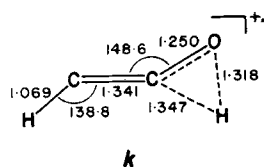
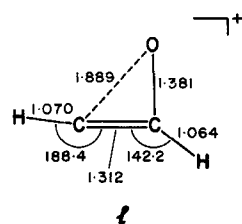


Figure 3. Schematic potential energy profile showing rearrangement pathways involving the hydroxyvinylidene (*e1*), ethynol (*b*) and ketene (*a*) radical cations.

1,2-hydrogen shift which interconverts the formylmethylene radical cation *f* and the ethynol radical cation *b*. The energy of *k* relative to *a* is 519 kJ mol^{-1} . A search for a transition structure representing the direct 1,3-hydrogen shift for the rearrangement of the ethynol radical cation (*b*) to the ketene radical cation (*a*) was unsuccessful. The calculations indicate that dissociation to give H^\bullet and $[\text{H}-\text{C}=\text{C}=\text{O}]^+$ (triplet) may be preferred. In the absence of a direct pathway for $b \rightarrow a$, the rearrangement $b \rightarrow f \rightarrow a$ provides an estimate for the barrier separating *b* from *a* (Fig. 3), and at 330 kJ mol^{-1} is found to be substantial.

At the HF/3-21G level, the oxirene radical cation of C_s symmetry (*c2*) was found to be preferred over the species with C_{2v} symmetry (*c1*). A transition structure *l*



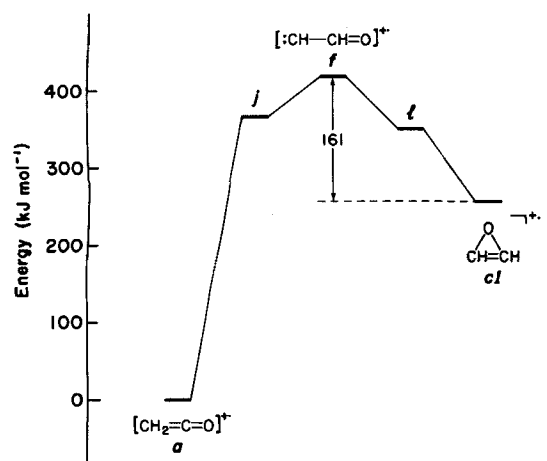
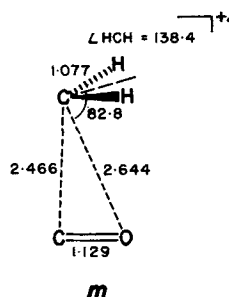


Figure 4. Schematic potential energy profile showing the rearrangement pathway from the oxirene (*c1*) to the ketene (*a*) radical cation.

was determined for the rearrangement of the formylmethylene radical cation (*f*) to (*c2*). But whereas *c1*, *c2*, *f* and *l* are all very close in energy at the HF/3-21G level, at higher levels of theory ion *f* and associated transition structures *j* and *l* are substantially higher in energy than *c1*. As a transition structure for a direct rearrangement of *c1* to *a* was not found, the pathway via *f*, i.e. $c1 \rightarrow f \rightarrow a$, provides our best estimate (161 kJ mol⁻¹) for the barrier separating *c1* from *a* (Fig. 4).

Transition structure *m* corresponds to the 1,2-CH₂



shift which converts $[\text{:C=O-CH}_2]^{+\bullet}$ (*d*) into $[\text{CH}_2=\text{C=O}]^{+\bullet}$ (*a*). The calculated energy of *m* relative to *d* gives a barrier of 93 kJ mol⁻¹ for this rearrangement. It should be noted that this energy is close to the dissociation energy for $d \rightarrow \text{CO} + [\text{CH}_2]^{+\bullet}$ (111 kJ mol⁻¹), consistent with the long C---C and C---O distances in *m*. Our calculations show that both *a* and *d* can dissociate to give CO and $[\text{CH}_2]^{+\bullet}$ without reverse activation energy, a result which for *a* is in accord with the experimental observation that at threshold the dissociation occurs with zero kinetic energy release.¹⁶⁻¹⁸ We note in this respect also that $[\text{CH}_2=\text{C=O}]^{+\bullet}$ (*a*), upon distortion to C_s symmetry (from C_{2v}), can lead to ground state $[\text{CH}_2]^{+\bullet}$ (²A₁) and need not go to $[\text{CH}_2]^{+\bullet}$ (²Π) as has been suggested recently.²¹ Our calculated dissociation energy for $a \rightarrow \text{CO} + [\text{CH}_2]^{+\bullet}$ of 370 kJ mol⁻¹ may be compared with an experimental value of 399 kJ mol⁻¹ based on the heats of formation (ΔH_f^0) of 885, -114 and 1398 kJ mol⁻¹ for $[\text{CH}_2=\text{C=O}]^{+\bullet}$ (*a*),[†] C=O ³⁷ and

[†] The reported heat of formation³⁷ for $[\text{CH}_2=\text{C=O}]^{+\bullet}$ of 871 kJ mol⁻¹ has been adjusted in line with recent redeterminations^{9,38} of the heat of formation of ketene.³⁹

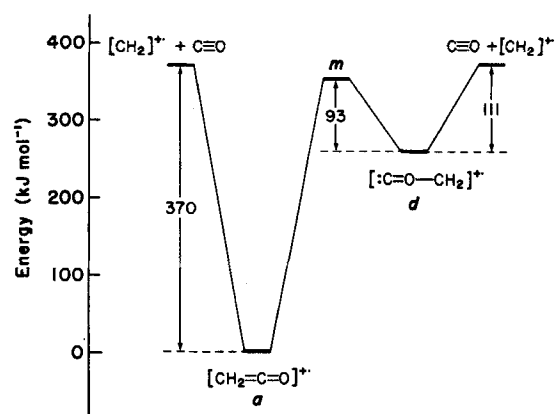
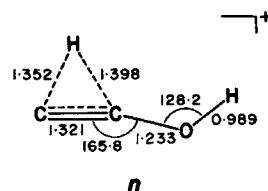


Figure 5. Schematic potential energy profile showing the relative stabilities of $[\text{CH}_2=\text{C=O}]^{+\bullet}$ (*a*) and $[\text{:C=O-CH}_2]^{+\bullet}$ (*d*).

$[\text{CH}_2]^{+\bullet}$,³⁷ respectively. The resulting potential energy profile (Fig. 5) illustrates the existence of *d* in a potential energy well of moderate depth.

Finally, we have also considered the rearrangement of the hydroxyvinylidene radical cation, *e*, to the more stable ethynol radical cation, *b*. The transition structure for the 1,2-hydrogen shift, *n*, is calculated to lie



136 kJ mol⁻¹ higher than *e* at the HF/3-21G level. Our best calculations, however, show that this energy is substantially reduced, yielding a barrier for $e \rightarrow b$ of only 35 kJ mol⁻¹ (see Fig. 3). The rearrangement of $e \rightarrow b$ may be compared with the related vinylidene \rightarrow acetylene isomerisation ($\text{CH}_2=\text{C:} \rightarrow \text{CH}\equiv\text{CH}$), for which it was found that the relatively small barrier calculated at the MP3/6-31G* level (29 kJ mol⁻¹ after zero-point correction) reduces to near-zero when determined at still higher levels of theory.⁴⁰

CONCLUSIONS

The following conclusions emerge from this study.

- The global minimum on the $[\text{C}_2\text{H}_2\text{O}]^{+\bullet}$ potential energy surface is the ketene radical cation (*a*).
- Three additional $[\text{C}_2\text{H}_2\text{O}]^{+\bullet}$ isomers are predicted to be stable, observable ion species. These are the ethynol radical cation (*b*), the oxirene radical cation (*c*) and a structure $[\text{:C=O-CH}_2]^{+\bullet}$ (*d*) which resembles a complex of CO with $[\text{CH}_2]^{+\bullet}$. The calculated energies are 189, 257 and 259 kJ mol⁻¹, respectively, above that of the ketene radical cation (*a*).
- The hydroxyvinylidene radical cation (*e*), lying 376 kJ mol⁻¹ above *a*, requires little energy for rearrangement to the ethynol radical cation (*b*), and is unlikely to be observable.

- (iv) The formylmethylene radical cation (f) is unstable, and may rearrange with little or no barrier to a or c.
- (v) Both $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ (a) and $[\text{:C}=\text{O}-\text{CH}_2]^{+\bullet}$ (d) may dissociate to CO and $[\text{CH}_2]^{+\bullet}$ without reverse activation energy.
- (vi) Finally, we note that the neutral parents of ions b, c and d have not yet been prepared experimentally and the ions will therefore have to be

generated in an indirect manner via fragmentation and/or rearrangement of suitable precursor ions, or via ion/molecule reactions.

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