Theoretical Study on the Isomerization and Dissociation of $C_4H_4O^{+\cdot}$ Radical Cation

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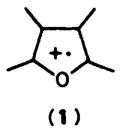
A MINDO/3 theoretical study has been performed on the potential surface of the $C_4H_4O^{+\cdot}$ radical cation. Fragmentations yielding $C_3H_4^{+\cdot}$ (CO loss), $C_3H_3^+$ (CHO loss), and $C_2H_2O^{+\cdot}$ (C_2H_2 loss) ions have been studied. A wide number of pseudostable species have been found. Very complex rearrangements occur previous to the fragmentations. Kinetic aspects are discussed.

In recent years, considerable progress has been made in understanding the unimolecular decomposition of radical cations, since a large number of techniques complementary to mass spectrometry, such as collisional activation[1] or photoion–photoelectron coincidence techniques,[2] can now be used to give a detailed description of the corresponding fragmentation mechanisms. In spite of this, a large number of decomposition pathways are still controversial, owing in part to the fact that, in general, many isomeric structures of gas-phase radical cations, not observed in the neutral parent molecules, can be stable entities, and so analogies with the reactivity of the neutral species can seldom be drawn. The $C_4H_4O^{+\cdot}$ radical cation belongs to this group. This cation can be generated from a wide number of neutral precursors, yielding different isomers: the loss of CO in 2-pyrone, for instance, produces a $C_4H_4O^{+\cdot}$ ion, the structure of which [furan-like (**1**) or not?] has led to a large number of reports.[3–9] The structure and decomposition products of $C_4H_4O^{+\cdot}$ ions obtained from furan and other precursors have also been investigated,[10,11] and a wide number of isomeric $C_4H_4O^{+\cdot}$ ions have been obtained and characterized.[12] Vinylketene (**2**) seems to be the most stable of these ions,[10,12] but the relative abundance of the peaks corresponding to *m/z* 39 (HCO loss), 40 (CO loss), and 42 (C_2H_2 loss) is different in ions generated from different neutral precursors furan, 2-pyrone, and vinylketene, leading to the conclusion that the fragmentation mechanisms do not have the same limiting step. Willett and Baer[11] have concluded, by absolute rate measurements at selected furan ion internal energies, that the isomerization is slower than the CO loss, and have carried out RRKM calculations in order to obtain insight into the nature of the limiting transition state, but no conclusive information on this structure has been put forward, nor on the possible intermediate products.

Quantum mechanical methods have proved to be a good tool in the mechanism elucidation of simple radical cation systems.[13–17] Once the potential surface is well known, and the stationary points well characterized, the reaction rate constants can easily be determined from the calculated vibrational frequencies and activation energies. We report here a theoretical study of $C_4H_4O^{+\cdot}$ radical cation rearrangements and fragmentations, yielding $C_3H_4^{+\cdot}$, $C_3H_3^+$, and $C_2H_2O^{+\cdot}$, by loss of CO, HCO, and C_2H_2, respectively.

Computational Details

The calculations reported here have been carried out by the MINDO/3 method, with standard parameters,[18] since this has proved to give reasonable results for a wide variety of radical cation studies,[13,17] and has been shown to reproduce vibrational frequencies quite well.[19] Open-shell species have been calculated at the UHF level. Geometries have been optimized without restrictions, with the McIver and Komornicki algorithm.[20] All stationary points of the potential surface have been characterized by diagonalizing the hessian matrix. The vibrational frequencies have been calculated from the force constant matrix by using classical methods.[21]



(**1**)

$H_2C—CH—CH—CO^{+\cdot}$

(**2**)

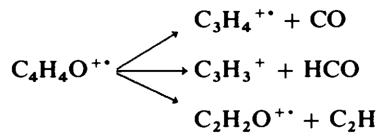
The rate–energy dependence for unimolecular reactions is given by equation (1)[22] where σ is the reaction path degeneracy

$$k(E) = \sigma G^*(E - E_0)/hN(E)\ (E \geqslant E_0) \qquad (1)$$

and E_0 is the reaction critical energy. $N(E)$ is the states density in the reactant at energy E, and $G^*(E - E_0)$ refers to the integrated states density at energy $E - E_0$. $N(E)$ and $G^*(E - E_0)$ are calculated from the rigid rotor–harmonic oscillator approximation.[23]

Results and Discussion

(1) *Potential Surface Description.*—The calculations have led to a high number of minima and transition states, with a wide number of isomerization possibilities. In order to clarify the description of the potential surface, we will present only the main rearrangements leading to three decomposition processes, loss of CO, of CHO, and of C_2H_2:



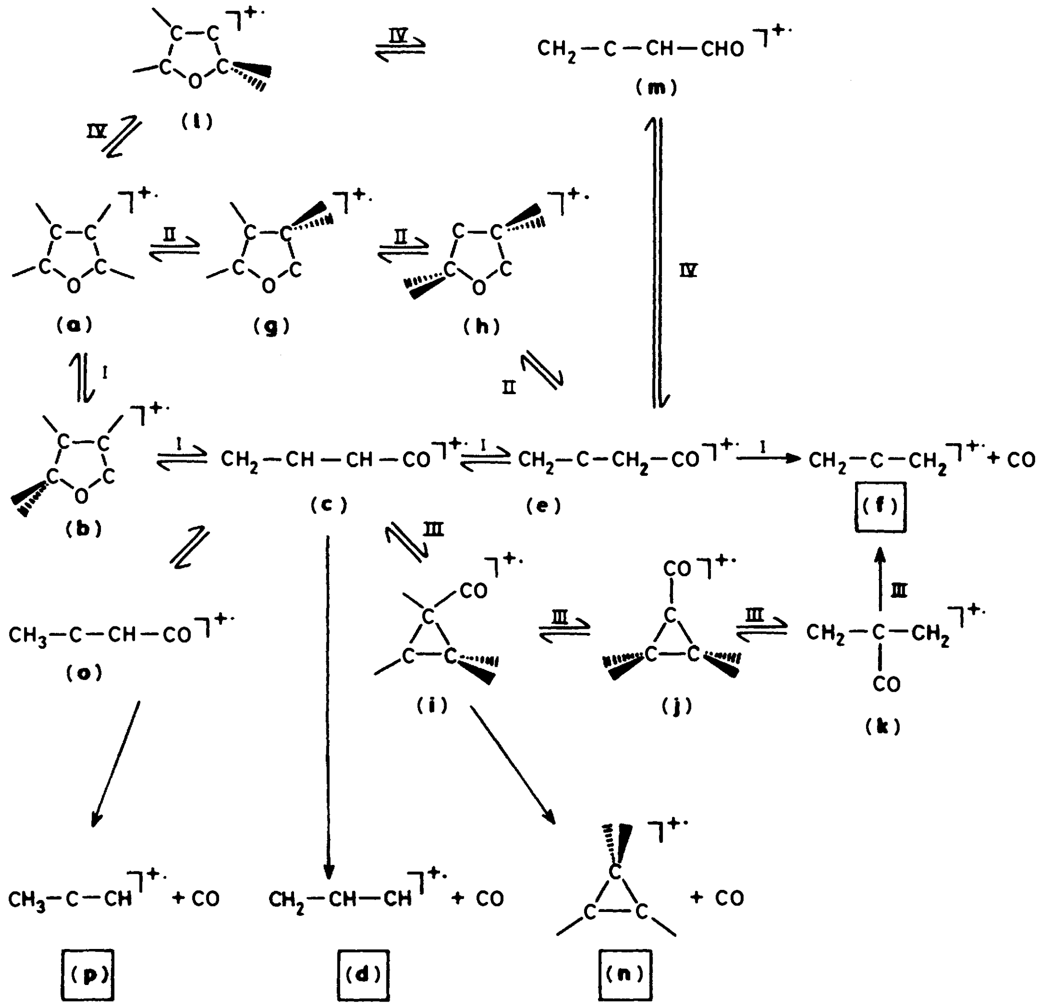
$C_4H_4O^{+\cdot} \rightarrow C_3H_4^{+\cdot} + CO$

$C_4H_4O^{+\cdot} \rightarrow C_3H_3^{+} + HCO$

$C_4H_4O^{+\cdot} \rightarrow C_2H_2O^{+\cdot} + C_2H_2$

Loss of CO. This fragmentation process has been found to be the most complex, because there are several alternative ways of isomerization of furan$^{+\cdot}$ (**a**) before losing CO to give allene$^{+\cdot}$ (**f**), but other $C_3H_4^{+\cdot}$ isomers can also be obtained: propenylidene$^{+\cdot}$ (**d**), cyclopropene$^{+\cdot}$ (**n**), and propyne$^{+\cdot}$ (**p**), as shown in Scheme 1.

(i) Formation of allene$^{+\cdot}$. Two alternative ways of obtaining allene$^{+\cdot}$ from furan$^{+\cdot}$ have already been presented as preliminary results for $C_4H_4O^{+\cdot}$ fragmentation processes.[24] The energy profiles of both isomerizations (paths I and II) are shown in Figure 1. A third path with a different isomerization scheme has been found, called path III in Figure 1 and Scheme 1. The fragmentation step implies roughly the same energy in the different mechanisms, the relative energies of the corresponding



Scheme 1.

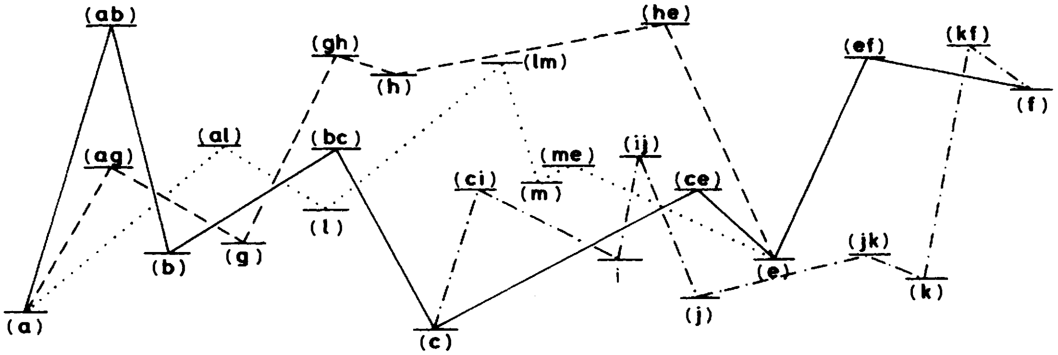


Figure 1. Energy profile of $C_4H_4O^{+\cdot}$ isomerizations and CO loss to give allene$^{+\cdot}$, obtained by MINDO/3: —— path I; – – – path II; –·– path III; ···· path IV

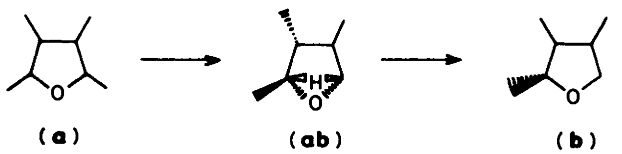
transition states being 72.4 kcal mol^{-1} in structure (**ef**) (paths I and II), and 75.5 kcal mol^{-1} in structure (**kf**) (path III). Energies are reported in Table 1.

A fourth possibility, path IV in Scheme 1 and in Figure 1, has been found after a more exhaustive analysis of the potential surface. In this case, the highest energy required in the isomerizations preceeding the decomposition step is 71.6 kcal mol^{-1} [structure (**lm**)], slightly below the fragmentation energy of the transition state (**ef**).

Path I (see Scheme 1) occurs *via* vinylketene$^{+\cdot}$ (**c**) which is the most stable isomer found (the *trans*-form is 1.2 kcal mol^{-1} more stable than the *cis*), as previously reported,[25] by 5.9 kcal mol^{-1} with respect to furan$^{+\cdot}$ (**a**) in agreement with experience.[10] Furan$^{+\cdot}$ rearranges to vinylketene$^{+\cdot}$ through intermediate (**b**), 21.3 kcal mol^{-1} less stable than (**c**), obtained by a [1,4]hydrogen migration in furan$^{+\cdot}$. The major geometrical changes in (**b**), with respect to furan$^{+\cdot}$, are in agreement with the rearrangement of the π system: lengthening of the H_2C–CH

Table 1. Relative energies (kcal mol^{-1}) of stationary points of the $C_4H_4O^{+\cdot}$ radical cation potential surface, referred to *trans*-vinylketene$^{+\cdot}$, obtained by the MINDO/3 method, involved in CO, HCO, and C_2H_2 loss processes

Stationary point	Relative energy	Stationary point	Relative energy
(**a**) furan$^{+\cdot}$	5.9	(**ab**)	82.2
(**b**)	21.3	(**ag**)	44.7
(**c**) *cis*-vinylketene$^{+\cdot}$	1.2	(**al**)	50.0
trans-vinylketene$^{+\cdot}$	0.0	(**bc**)	48.8
(**d**) CO + propenylidene$^{+\cdot}$	87.8	(**cd**)	93.6
(**e**)	17.2	(**ce**)	37.1
(**f**) CO + allene$^{+\cdot}$	63.6	(**ci**)	37.1
(**g**)	23.9	(**co**)	28.5
(**h**)	68.2	(**ef**)	72.4
(**i**)	18.5	(**gh**)	73.6
(**j**)	8.1	(**gu**)	57.5
(**k**)	13.0	(**he**)	80.4
(**l**)	32.3	(**ij**)	46.1
(**m**) allenealdehyde$^{+\cdot}$	39.5	(**in**)	89.4
(**n**) CO + cyclopropene$^{+\cdot}$	80.8	(**iq**)	56.8
(**o**)	1.3	(**jk**)	19.5
(**p**) CO + propyne$^{+\cdot}$	77.5	(**kf**)	75.5
(**q**)	48.6	(**lm**)	71.6
(**r**)	60.4	(**me**)	43.9
(**s**) HCO + cyclopropenium^{+}	71.6	(**mt**)	90.7
(**t**)	87.9	(**op**)	83.0
(**u**)	28.5	(**qr**)	67.7
(**v**)	70.7	(**rs**)	84.1
		(**uv**)	75.1

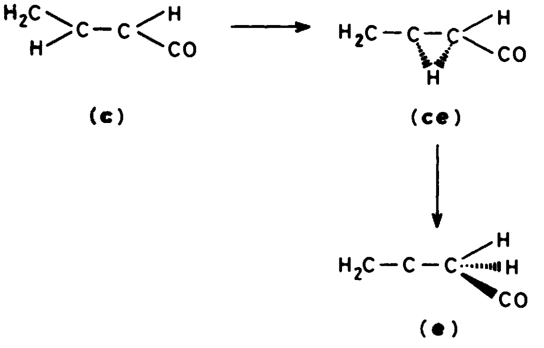


(**a**) (**ab**) (**b**)

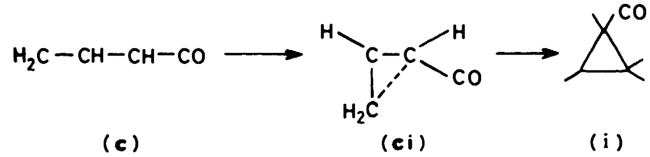
and H_2C–O bonds (1.504 and 1.421 Å, respectively, in place of 1.431 and 1.324 Å in furan$^{+\cdot}$*), and shortening of the C–O and HC–CH bonds (1.293 and 1.368 Å, compared with 1.324 and 1.393 Å in furan$^{+\cdot}$). The corresponding transition state (**ab**) has a relative energy of 82.2 kcal mol^{-1}, which implies a high activation energy, 76.3 kcal mol^{-1}, from furan$^{+\cdot}$, and is thus the energetically limiting step of the mechanism. The migrating hydrogen is bridged between the two α-carbons of furan$^{+\cdot}$, with a loss of planarity of the ring structure. The bridged hydrogen bond lengths are HC–H, 1.361, and C–H, 1.322 Å. The intermediate (**b**) isomerizes to vinylketene$^{+\cdot}$ (**c**) by simple breaking of the H_2C–O bond. The corresponding transition state (**bc**) has a relative energy of 48.8 kcal mol^{-1}. The structure is mostly reactant-like, with a breaking H_2C–O bond length of 1.941 Å.

From vinylketene$^{+\cdot}$ (**c**) two alternative isomerization paths are possible before CO loss, as shown in Scheme 1: path I, with only hydrogen migration before formation of the allene$^{+\cdot}$ (**f**), and path III, which implies three-centred cyclic structures. Both paths are roughly equivalent, from an energetic point of view, as appears from Figure 1.

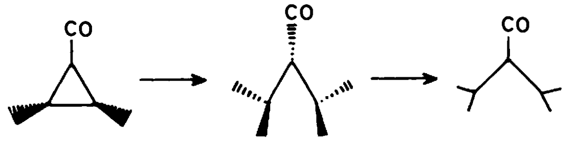
In path I, vinylketene$^{+\cdot}$ (**c**) isomerizes to (**e**) by a [1,2]-hydrogen shift. (**e**) Has a relative energy of 17.2 kcal mol^{-1}, with a slightly bent structure (H_2C–C–CH_2CO angle, 156.5°; H_2C–C bond length, 1.299; C–CH_2CO, 1.446; HC–CO, 1.445; C–O, 1.128 Å). This isomerization does not need a high activation energy: the corresponding transition state (**ce**) has a relative energy of 37.1 kcal mol^{-1}. The bridged hydrogen bond lengths are CH_2C–H, 1.587, and COCH–H, 1.170 Å. The intermediate (**e**) loses CO by simple H_2C–CO bond breaking, giving allene$^{+\cdot}$ and CO. The product (**f**) has a relative energy of 63.6 kcal mol^{-1}, and the fragmentation transition state (**ef**) of 72.4 kcal mol^{-1}. The H_2C–CO bond length, 2.629 Å, shows its strong product-like character.



(**c**) (**ce**) (**e**)



(**c**) (**ci**) (**i**)



(**j**) (**jk**) (**k**)

On the other hand, path III implies more isomerization steps before losing CO (see Scheme 1). The first one is the cyclization of vinylketene$^{+\cdot}$ (**c**) to (**i**), the energy of which lies 18.5 kcal mol^{-1} above *trans*-vinylketene$^{+\cdot}$, through the transition state (**ci**), with an activation energy of 35.9 kcal mol^{-1} from *cis*-vinylketene$^{+\cdot}$ (see Figure 1 and Table 1). The most relevant geometrical parameters of (**i**) are the C–C bond lengths: H_2C–CH, 1.433; H_2C–CHCO, 1.555; HC–CHCO, 1.510; HC–CO, 1.407 Å, with the hydrogen atoms lying out of the ring plane. In the transition state, structure (**ci**), the newly forming bond, H_2C–CHCO, has length 1.934 Å. The intermediate (**i**) isomerizes to (**j**), a quite stable intermediate with a relative energy of 8.1 kcal mol^{-1}, by an α–β hydrogen migration. (**j**) Has a C_{2v} geometry (H_2C–CH_2 bond length, 1.486; H_2C–CCO, 1.491 Å). The stability of this isomer is in qualitative agreement with the experimental heat of formation estimated by Holmes *et al.*[12] to be 4 ± 2 kcal mol^{-1} higher than that of vinylketene$^{+\cdot}$. The corresponding transition state (**ij**) has a relative energy of 46.1 kcal mol^{-1}, with the migrating hydrogen in a bridged position (HC–H, 1.314! COC–H, 1.268 Å). (**j**) Easily isomerizes to (**k**), of relative energy 13.0 kcal mol^{-1} and C_{2v} geometry (H_2C–C bond length, 1.403 Å; COC–C, 1.426; C–O, 1.129 Å; C–C–C angle, 127.3°) through the transition state (**jk**), of relative energy 19.5 kcal mol^{-1}, which has a non-symmetric structure, with a breaking C–C bond length of 1.971 Å, and two non-equivalent H_2C–CCO bond lengths, 1.350 and 1.454 Å, respectively. The (**jk**) structure can be interpreted in terms of molecular orbitals of the reactant (**j**) and the product (**k**), as in other cyclopropyl structural rearrangements, such as bicyclo-

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* All the geometries of minima and transition states, as well as the vibrational frequencies, are available, if requested.

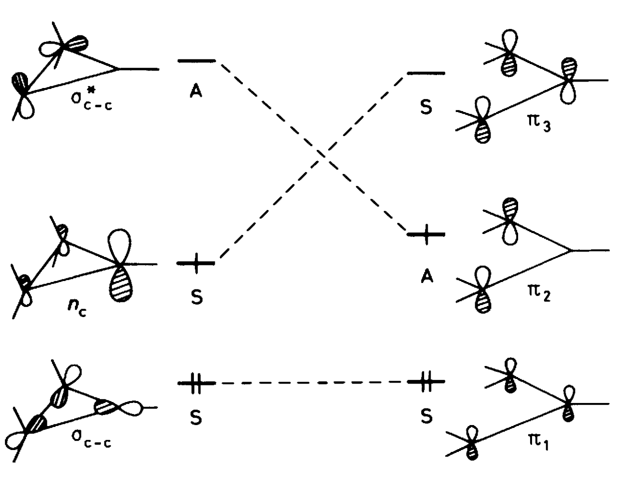
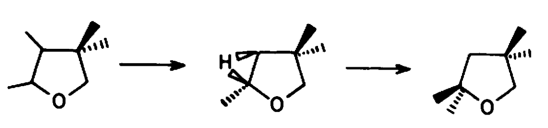
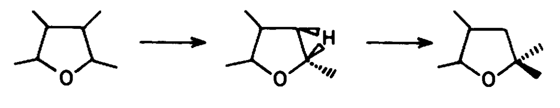


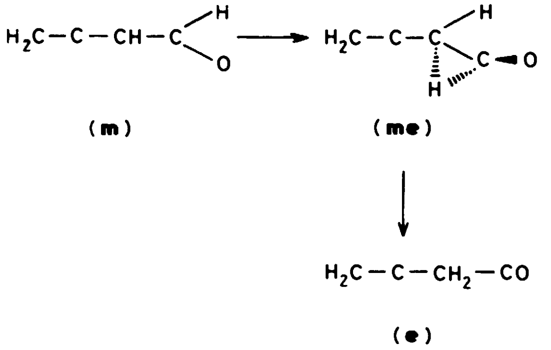
Figure 2.



(g) (gh) (h)



(a) (al) (l)



butyl to cyclobutenyl radical.[26] Both reactant and product have C_{2v} symmetry. Figure 2 shows the molecular orbital correlation between both structures. If the symmetry plane bisecting the C–C bond is conserved along the reaction, the SOMO of (**j**), a symmetric π orbital, almost n_c, correlates with the LUMO of (**k**), *i.e.*, the reactant correlates with an excited state of the product. Thus, the rearrangement must proceed through a non-symmetric path. The two H_2C–CCO bond lengths of the transition state (**jk**) have comparable values with those found in other ring openings of cyclopropyl structures.[26] (**k**) Loses CO giving allene$^{+\cdot}$ with a high activation energy, since the corresponding transition state (**kf**) (C–CO bond length 2.560 Å) lies 75.5 kcal mol^{-1} above vinylketene$^{+\cdot}$.

Path II is an alternative isomerization, occurring *via* two consecutive [1,2] hydrogen migrations in furan$^{+\cdot}$, to give the intermediate (**e**). The first intermediate (**g**) in this rearrangement is obtained by an α–β hydrogen transposition in furan$^{+\cdot}$, with similar stability to intermediate (**b**), 23.9 kcal mol^{-1} relative to *trans*-vinylketene$^{+\cdot}$. As in (**b**), the main geometric changes correspond to π-system reorganization (HC–O bond length, 1.401; C–O, 1.229; H_2C–C, 1.483; H_2C–CH, 1.514; HC–CH, 1.350 Å). In the corresponding transition state, (**ag**) with a relative energy of 44.7 kcal mol^{-1}, the migrating hydrogen atom is bridged between the two carbon atoms (OC–H, 1.247; HC–H, 1.416 Å). The next step, another [1,2]hydrogen shift, leads to (**h**), the cyclic precursor of (**e**), a rather unstable isomer, 68.2 kcal mol^{-1} over vinylketene$^{+\cdot}$ (H_2C–O, 1.432; C–O, 1.227; H_2C–CO, 1.490; C–CH_2CO, 1.476; C–CH_2, 1.482 Å). The energy of the related transition state (**gh**) is 73.6 kcal mol^{-1}, mostly product-like (HC–H, 1.182; C–H, 1.572 Å). Ring opening giving (**e**) is the energy-determining step of this possible mechanism. The corresponding transition state (**he**) has a relative energy of 80.4 kcal mol^{-1}. As expected from the energy values, the structure of (**he**) is strongly reactant-like, with a breaking C–O bond length of 1.843 Å.

Finally, in Path IV, furan$^{+\cdot}$ (**a**) isomerizes by a β–α hydrogen migration to (**l**), which opens to give allenealdehyde$^{+\cdot}$ (**m**), the precursor of (**e**). The intermediate (**l**) has an energy of 32.3 kcal mol^{-1} above vinylketene$^{+\cdot}$, and the geometrical parameters are in agreement with π-system modifications: HC–O, 1.284; H_2C–O, 1.411; HC–C, 1.356; H_2C–C, 1.469 Å. The corresponding transition state, (**al**), has a relative energy of 50.0 kcal mol^{-1}, with the bridged hydrogen atom closer to the product structure: HC–H, 1.281; C–H, 1.352 Å. The next step, ring opening, gives allenealdehyde$^{+\cdot}$ (**m**) with a relative energy of 39.5 kcal mol^{-1}, which agrees quite well with the experimentally estimated relative energy of this species,[12] 42 kcal mol^{-1} less stable than vinylketene$^{+\cdot}$. In this structure, the H_2C–C and C–CH bond lengths are almost equivalent, 1.323 and 1.329 Å; HC–COH, 1.495 Å. The (**l**) ⟶ (**m**) ring opening is the limiting step of the (**a**) ⟶ (**e**) transformation in this mechanism, with a transition state (**lm**), relative energy of 71.6 kcal mol^{-1}. The breaking H_2C–O bond is 2.140 Å long, in accord with high product-like character, as expected from the energy values.* From (**m**), the aldehyde hydrogen atom migrates to the α-carbon to give (**e**). The corresponding transition state (**me**), with a relative energy of 43.9 kcal mol^{-1}, is strongly reactant-like: OC–H, 1.242; HC–H, 1.529 Å.

The described isomerization paths from furan$^{+\cdot}$ giving finally allene$^{+\cdot}$ + CO (**f**) and the related energy values show that three of them, paths I and II, previously described,[24] and path III, involve a thermodynamically limiting isomerization step, which requires *ca.* 80 kcal mol^{-1}, in front of the fragmentation step, which requires 72.4 kcal mol^{-1}. In path IV isomerization to (**e**) requires an energy of 71.6 kcal mol^{-1}, referred to vinylketene$^{+\cdot}$. The loss of CO from furan$^{+\cdot}$ at low ion internal energies seems thus more likely to occur *via* path IV, which does not require higher activation energy than the fragmentation step, in contrast to our preliminary conclusions.[24] The difference between the energies of the two transition states (**lm**) and (**ef**), of 0.8 kcal mol^{-1}, is to be considered within the limits of precision of the method of calculation. By comparing our calculated energies and the experimentally known heats of formation, we estimate that they are in general in good agreement, with the exception of the CO-loss product (**f**) which lies *ca.* 15 kcal mol^{-1} above the experimental energy, owing to the incorrect MINDO/3 estimation of the CO heat of formation, −13.5 kcal mol^{-1},[18] instead of −26.4 kcal mol^{-1} found by experience,[28] which gives a relative energy for products (**f**) of 63.6 kcal mol^{-1}, instead of 49.0 kcal mol^{-1} from

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* No linear intermediate of the type CH–CH–CH–CHO$^{+\cdot}$ between (**a**) and (**m**), as proposed in ref. 27, has been found, since all attempts at minimizing such a structure have led to (**m**), by hydrogen migration.

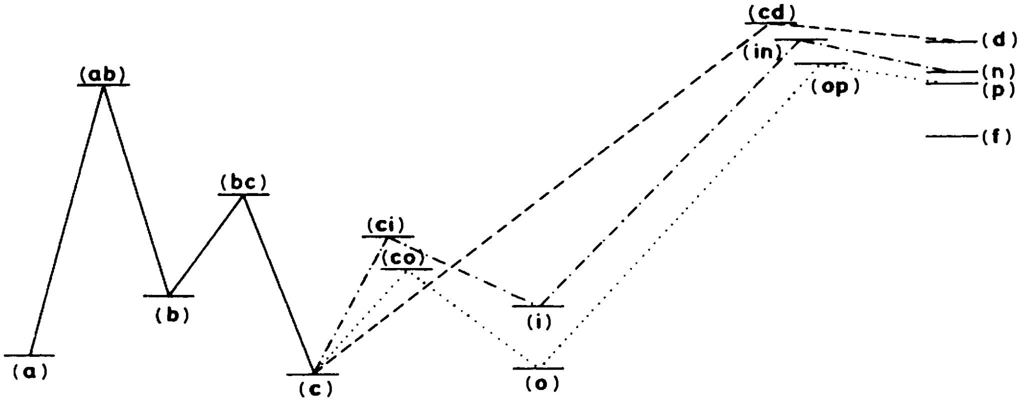
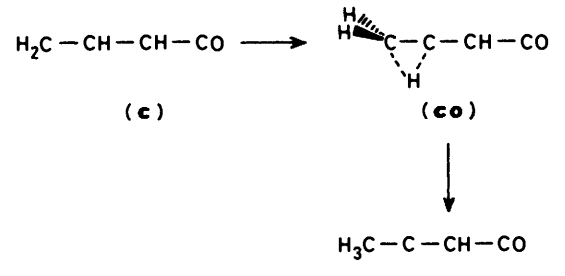


Figure 3. Energy profile of $C_4H_4O^{+\cdot}$ isomerizations and CO loss to give propenylidene$^{+\cdot}$ (– – –), cyclopropene$^{+\cdot}$ (– • –), and methylacetylene$^{+\cdot}$ (• • •), obtained by MINDO/3



(**c**) (**co**) (**o**)

experiment.[28,29] From this consideration, we infer that the energy of the fragmentation transition state (**ef**), strongly product-like (C–CO, 2.629 Å), is somewhat overestimated, and that (**lm**) is thus probably the energy-limiting transition state of the full process, according to experimental conclusions.[9,10] The energy involved, 71.6 kcal mol^{-1}, lies in the experimental range, 60—80 kcal mol^{-1}: 67.2 kcal mol^{-1}, determined by the difference between the appearance energy of $C_3H_4^{+\cdot}$ from furan[11] and the furan ionization potential,[11,30] but estimated to be *ca.* 80 kcal mol^{-1} from the work of Holmes and Terlouw.[9] Furthermore, this mechanism agrees with recent experimental results[27] on [2,5-$^2H_2$]furan$^{+\cdot}$, which mostly gives CHD–C–CHD$^{+\cdot}$ by CO loss. MNDO and 3-21G calculations have also been performed by these authors. Since no results are reported for fragmentation steps, and no characterization of stationary points, specially transition states, is reported, comparisons between both sets of results can hardly be done, except that our transition state energies are significantly lower, by 20—50 kcal mol^{-1}, owing probably in part to the refining of the stationary points by means of the McIver–Komornicki algorithm.[20] Kinetic considerations will be discussed below.

At higher ion internal energies, all the isomerization paths become competitive, and allene$^{+\cdot}$ can be generated *via* parallel paths.

(ii) Other C_3H_4 isomers. As shown in Scheme 1, other $C_3H_4^{+\cdot}$ isomers can be generated by CO loss from $C_4H_4O^{+\cdot}$: propenylidene$^{+\cdot}$ (**d**), cyclopropene$^{+\cdot}$ (**n**), and propyne$^{+\cdot}$ (**p**). All these fragmentations occur *via* vinylketene$^{+\cdot}$ (**c**) and require more energy than the formation of allene$^{+\cdot}$. The energy profiles of these fragmentations are shown in Figure 3.

Propenylidene$^{+\cdot}$ (**d**) is obtained directly from vinylketene$^{+\cdot}$. In accord with the high energy of the product (**d**), 87.8 kcal mol^{-1}, 24.2 kcal mol^{-1} above allene$^{+\cdot}$ + CO (**f**), this decomposition needs a high activation energy, 93.6 kcal mol^{-1}. The transiton state structure (**cd**) is practically dissociated, the CH–CO bond length being 2.695 Å.

The formation of cyclopropene$^{+\cdot}$ (**n**) needs one isomerization step from vinylketene$^{+\cdot}$ to (**i**), before CO loss. The decomposition transition state (**in**) requires high energy: 89.4 kcal mol^{-1}, relative to vinylketene$^{+\cdot}$. Its structure is practically product-like, the CH–CO bond length being 2.605 Å. The product (**n**), cyclopropene$^{+\cdot}$ + CO, has a relative energy of 80.8 kcal mol^{-1}.

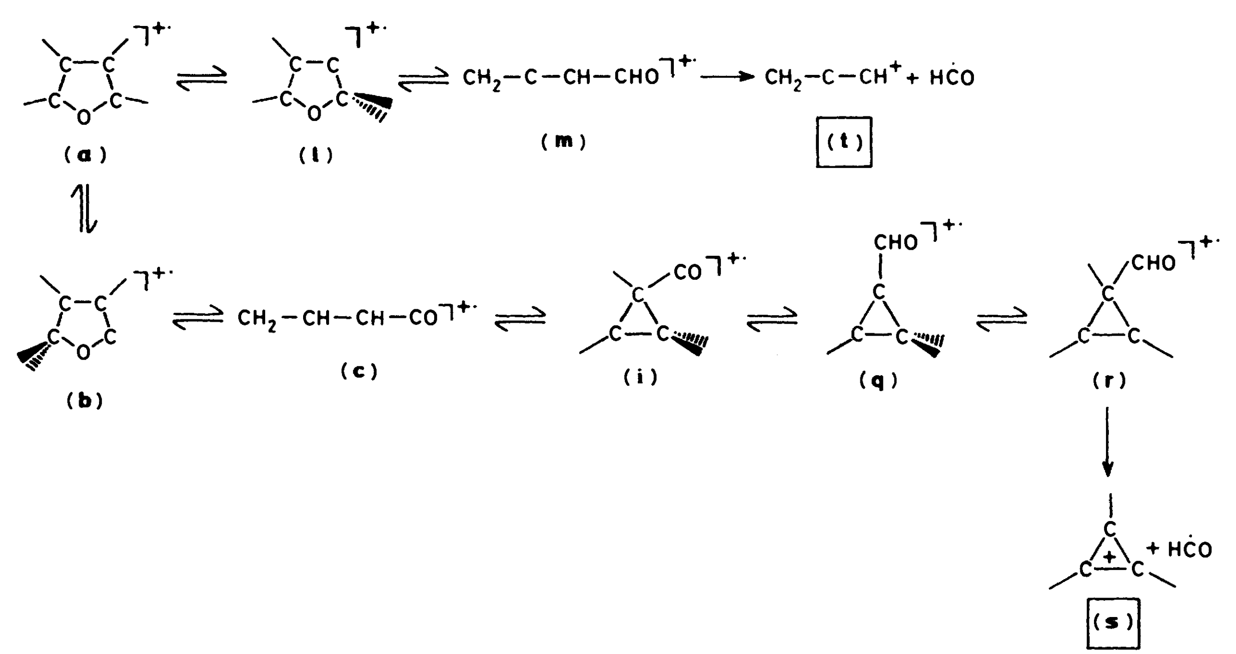
Finally, propyne$^{+\cdot}$ (**p**) is obtained from vinylketene$^{+\cdot}$ *via* the intermediate (**o**), obtained by a [1,2]hydrogen shift in vinylketene$^{+\cdot}$. It is a quite stable isomer, lying only 1.3 kcal mol^{-1} above (**c**). The transition state (**co**) has a relative energy of 28.5 kcal mol^{-1}.

From (**o**), CO loss requires high activation energy, the transition state, (**op**), lying 83.0 kcal mol^{-1} over vinylketene$^{+\cdot}$, with a practically dissociated structure: HC–CO bond length, 2.901 Å. The product propyne$^{+\cdot}$ + CO (**p**) has a relative energy of 77.5 kcal mol^{-1}. This calculated relative energy is higher by *ca.* 14 kcal mol^{-1} than the experimental value, estimated to be 63 kcal mol^{-1} above vinylketene$^{+\cdot}$,[28] owing to the error found in the MINDO/3 estimation of CO heat of formation, as discussed above. It suggests that the (**op**) transition-state energy is also overestimated by a similar amount, in considering its high product-like character. Thus, it can be concluded that, from furan$^{+\cdot}$, both fragmentation processes giving allene$^{+\cdot}$ and propyne$^{+\cdot}$ need energies of the same order, allowing them to be competitive, which is consistent with the wide range of kinetic energy released.[9] On the other hand, $C_3H_4^{+\cdot}$ fragments from vinylketene$^{+\cdot}$ have an appearance energy of 10.4 eV,[10] which, considering the heat of formation and the ionization potential of vinylketene$^{+\cdot}$,[10] is only compatible with the allene$^{+\cdot}$ structure, the lowest energy CO loss predicted by calculation.

Thus, propyne$^{+\cdot}$ is the most stable $C_3H_4^{+\cdot}$ isomer after allene$^{+\cdot}$. Propenylidene$^{+\cdot}$ (**d**) is the least stable of these isomers, by 24.2 kcal mol^{-1}. The energy required to obtain (**d**) and (**n**) is *ca.* 90 kcal mol^{-1}, higher by *ca.* 20 kcal mol^{-1} than allene$^{+\cdot}$.

Loss of HCO. Two possible $C_3H_3^+$ fragments can be obtained, as products of HCO loss from $C_4H_4O^{+\cdot}$ radical cation, as shown in Scheme 2. Both energy profiles are plotted in Figure 4.

The most stable of these products is the aromatic $C_3H_3^+$ cyclopropenium cation. This fragmentation occurs from furan$^{+\cdot}$ (**a**), vinylketene$^{+\cdot}$ (**c**), and the cyclic intermediate (**i**). (**i**) Isomerizes to the aldehyde (**q**) by a hydrogen shift. The intermediate (**q**) has an energy of 48.6 kcal mol^{-1} (bond lengths: H_2C–CH, 1.468; H_2C–CCOH, 1.525; HC–CCOH, 1.345; C–COH, 1.477 Å). The transition state (**iq**) lies 56.8 kcal mol^{-1} above vinylketene$^{+\cdot}$, with a predominantly product-like



Scheme 2.

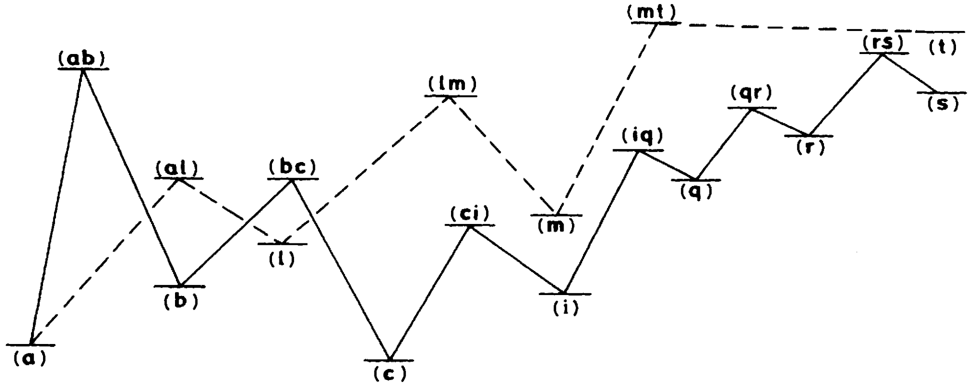
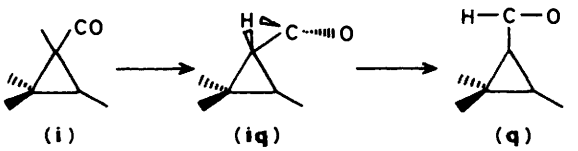
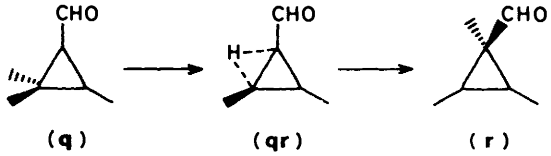


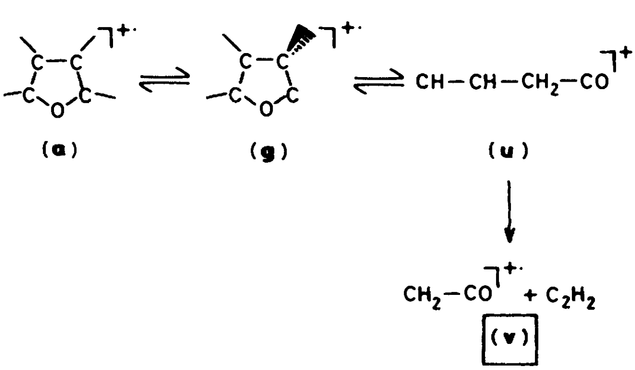
Figure 4. Energy profile of $C_4H_4O^{+\cdot}$ isomerizations and HCO loss to give $CH_2{=}CH^+$ (- - -) and cyclopropenium$^{+\cdot}$ (——), obtained by MINDO/3





structure (C–H bond length, 1.669; OC–H, 1.190 Å). (**q**) Isomerizes to cyclopropenecarbaldehyde$^{+\cdot}$ (**r**) by a [1,2]-hydrogen shift, with a relative energy of 60.4 kcal mol^{-1} (both HC–CCHO bond lengths almost equivalent, 1.466; HC–CH, 1.347; C–COH, 1.558 Å). The corresponding transition state (**qr**) has a relative energy of 67.7 kcal mol^{-1}, with the bridged hydrogen position closer to the product (**r**): HC–H, 1.232; CHOC–H, 1.329 Å. (**r**) Finally loses HCO, giving cyclopropenium ion $C_3H_3^+$. The product (**s**) has a relative energy of 71.6 kcal mol^{-1}. HCO loss is the thermodynamically limiting step of this fragmentation path, since the transition state (**rs**) lies 84.1 kcal mol^{-1} above vinylketene$^{+\cdot}$, with predominant product-like character (C–COH, 2.318 Å). By comparing this fragmentation path with CO loss to give allene$^{+\cdot}$ (**f**) *via* path IV, and by considering the above comments on the energy of (**ef**) and (**f**), HCO loss from furan$^{+\cdot}$ requires 12.5 kcal mol^{-1} more than CO loss, which is in quite good agreement with the experimental $C_3H_3^+$ appearance energy,[11] higher by 0.5 eV than that of $C_3H_4^{+\cdot}$. On the other hand, the energy of (**s**) product is estimated to be 71 kcal mol^{-1} higher than that of vinylketene$^{+\cdot}$,[11] in a very good agreement with our calculated value.

The second fragmentation path to give linear $C_3H_3^+$ ion requires more energy, in accord with the great instability of this product. The dissociation occurs from allenealdehyde$^{+\cdot}$ (**m**) previously described. The energy of the final product (**t**) is 87.9 kcal mol^{-1}. The required energy for the fragmentation, the transition state (**mt**) energy, is 90.7 kcal mol^{-1}.



Scheme 3.

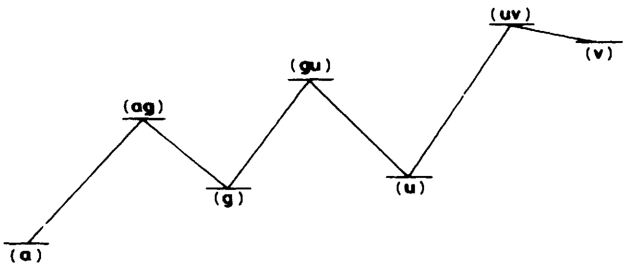
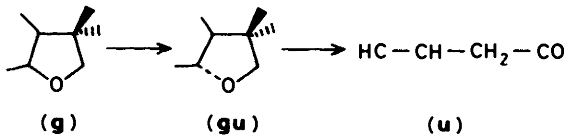


Figure 5. Energy profile of $C_4H_4O^{+\cdot}$ isomerizations involved in C_2H_2 loss, obtained by MINDO/3

Table 2. Rate constants[a] for the dissociation steps of the $C_4H_4O^{+\cdot}$ radical cation fragmentations at several ion energies (in eV)

Ion energy	$\log k_{(e)\longrightarrow(f)}$ (CO loss)	$\log k_{(u)\longrightarrow(v)}$ (C_2H_2 loss)	$\log k_{(r)\longrightarrow(s)}$ (HCO loss)
3.12	5.238 (4.845)	*b*	*b*
3.22	5.994 (5.110)	4.899 (3.109)	*b*
3.34	6.709 (5.437)	5.833 (4.667)	*b*
3.45	7.235 (5.771)	6.484 (5.186)	7.969 (3.771)
3.60	8.168 (6.581)	7.561 (6.086)	9.250 (4.881)

[a] Experimental values in parentheses. [b] Not observed experimentally at this ion energy.



Loss of C_2H_2. Only one path has been found for C_2H_2 loss, occurring *via* intermediate (g), previously described, as shown in Scheme 3. The energy profile is plotted in Figure 5.

The intermediate (g) isomerizes to (u) by breaking the HC–O bond. The linear product (u) has an energy of 28.5 kcal mol^{-1} relative to vinylketene$^{+\cdot}$. The main geometrical parameters of (u) are C–C bond lengths: HC–CH, 1.302; HC–CH$_2$, 1.502; H$_2$C–CO, 1.439 Å. The corresponding transition state (gu) has a relative energy of 57.5 kcal mol^{-1}. The breaking C–O bond length is 2.024 Å.

The intermediate (u) finally decomposes to give acetylene and $CH_2CO^{+\cdot}$ (v) with a relative energy of 70.7 kcal mol^{-1}. The corresponding transition state (uv) lies 75.1 kcal mol^{-1} above vinylketene$^{+\cdot}$, with a practically product-like structure (HC–CH$_2$ bond length, 2.629 Å). The energy required for this fragmentation process is 3.5 kcal mol^{-1} higher than CO loss, in agreement with the experimental difference[11] of 0.2 eV. This mechanism is also in agreement with that proposed by Bouchoux *et al.*,[27] from experimental and theoretical considerations.

In conclusion, it seems that the MINDO/3 theoretical description of the potential surface of $C_4H_4O^{+\cdot}$ gives energies for minima and transition states in quite good agreement with experimental data, except for the CO fragmentation, as discussed above. These calculations thus allow the fragmentation paths of this radical to be rationalized with a reasonable reliability.

(2) *Kinetic Considerations*.—From equation (1), it is easy to obtain the rate constants for the different steps of each fragmentation when the energies and vibrational frequencies of the minima and transition states are known. Table 2 shows the rate constants for the different dissociation steps studied. It appears that the calculated rate constants are higher than the experimental global ones for furan$^{+\cdot}$ decompositions.[11] Therefore, if the calculated values are similar, the corresponding isomerization before fragmentation should be slower than the dissociation step. But, when the minimum-energy paths are considered to lead to fragment precursors, (e) for CO loss, (r) for HCO loss, and (u) for C_2H_2 loss, no step with a smaller rate constant than the corresponding dissociation step is found. However, this does not mean that the global isomerization process is faster than fragmentation, because of its great complexity: there are parallel competitive reactions in several steps, and in some cases, the inverse rate constant is higher than the direct one. For example, in CO loss to give allene$^{+\cdot}$ from furan$^{+\cdot}$, at an ion energy of 3.12 eV, $\log k_{(a)\longrightarrow(l)} = 8.164$, whereas $\log k_{(l)\longrightarrow(a)} = 10.790$. To an approximation, by using the steady-state approximation for (a) $\longrightarrow$ (l) following path IV, without taking into account other branched reactions, the global isomerization constant rate is found to be lower than (e) $\longrightarrow$ (f) dissociation. Furthermore, competitive reactions will cause a decrease of the isomerization rate. Thus, in $C_4H_4O^{+\cdot}$ generated from furan$^{+\cdot}$, the great complexity of the rearrangement process previous to dissociation makes the 'isomerization step' the determining step of the CO, CHO, and C_2H_2 losses, without necessarily involving high isomerization energies.

A final consideration emerges from the above discussion. RRKM/QET calculations are often carried out by assuming vibrational frequencies of one minimum and one supposed transition state structure.[11] Conclusions built on such a reduction in the complexity of the potential surfaces should be prudently analysed, since they are hardly reliable.

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