[CH₃COH]·⁺, the Central Intermediate in the Isomerization–Dissociation Reactions of Ionized Vinyl Alcohol

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In complete agreement with experimental results ab initio molecular orbital calculations predict that ionized hydroxy(methyl)carbene, [CH₃COH]⁺, does not only exist as a stable $C_2H_4O^{·+}$ isomer but also serves as the key intermediate in the isomerization–dissociation processes of the cation radical of gaseous vinyl alcohol.

The keto–enol tautomerism of gaseous cation radicals has stimulated intense research activity of both experimentalists and theoreticians.[1] Collisional activation (C.A.) mass spectrometry, for example, revealed the existence of non-interconverting keto–enol ions in the gas phase, and thermochemical measurements demonstrated that ionized enols are substantially more stable than their tautomeric ketones.[1] This contrasts with the neutral systems in which, in general, a reversed order of stability exists.[2] Despite extensive research, experimental[3a–e] as well as theoretical,[3f,g] the detailed mechanism of the unimolecular decomposition of these ions

is not known even for the simplest case, i.e. the $C_2H_4O^{·+}$ ion. For $C_2H_4O^{·+}$ the following facts are known. The metastable molecular ions of both acetaldehyde (1) and vinyl alcohol (2) undergo unimolecular elimination of H·. Deuterium
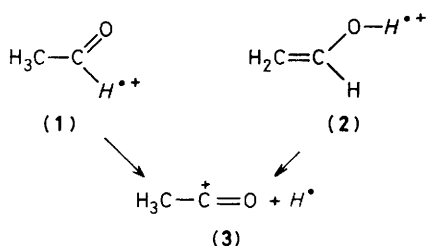
Scheme 1
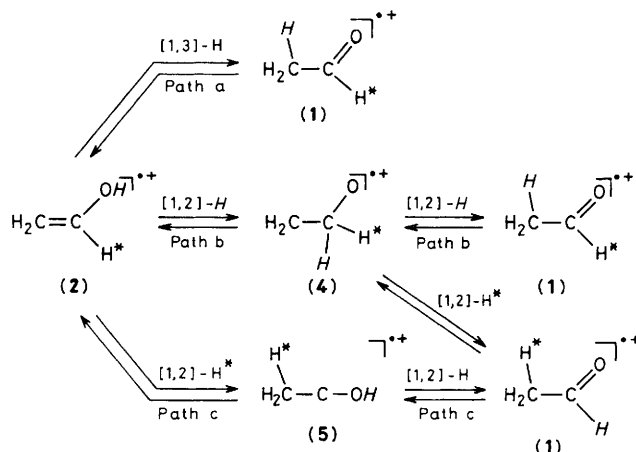
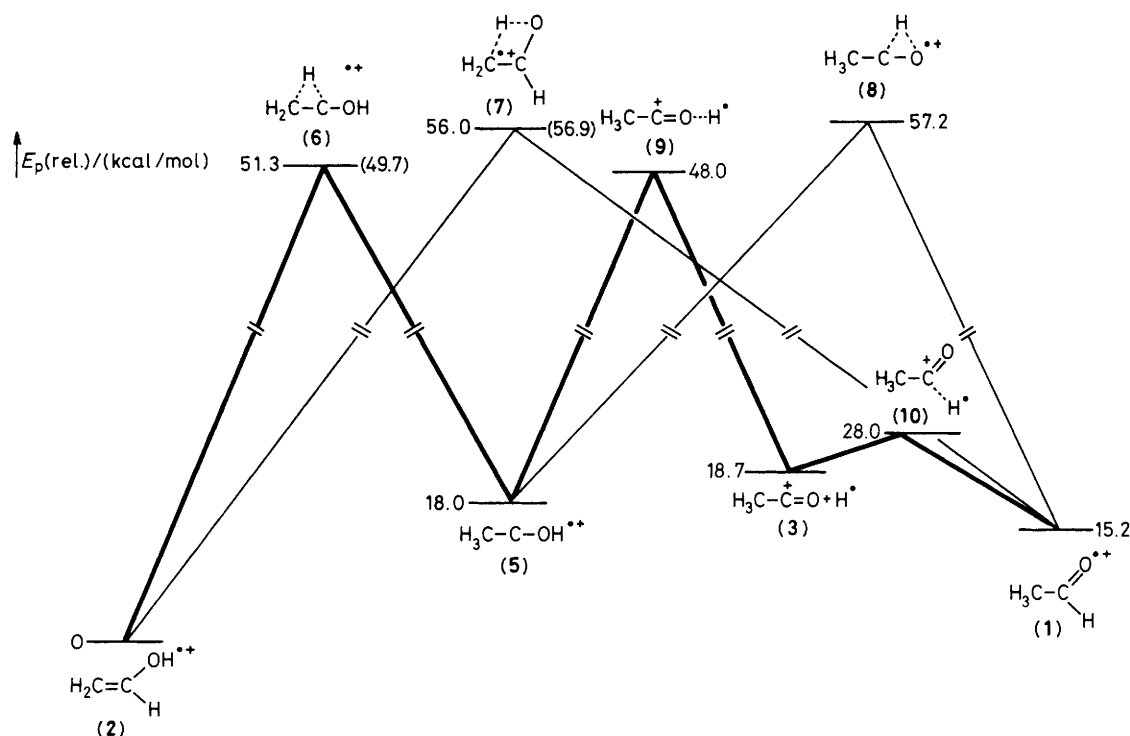Scheme 2. Possible mechanisms of the isomerization of (2) to (1).

Figure 1. Part of the potential energy surface of $C_2H_4O^{\cdot+}$ ions as calculated by MP3/6-31G*//4-31G [except for the transition state (10) which was calculated at the MP2 level]. Energy differences are given in kcal/mol and include corrections for zero-point energies. Numbers in parentheses give estimated relative energies at MP3/6-31G**/4-31G.

labelling experiments show[3b,4] that it is the hydrogen in italic type which is eliminated exclusively [Scheme 1]. The resulting $C_2H_3O^{\cdot+}$ ions were unambiguously identified as the acylium ion (3).[5]

However, several questions remained unsolved (Scheme 2). (i) Does (2) isomerize to (excited) (1) prior to H· loss? If so, does this process occur via a direct [1,3]hydrogen shift (path a) or by a combination of two consecutive [1,2]hydrogen migrations (paths b and c)? If the latter occurs, which hydrogen of (2) migrates initially, i.e. is it the one bonded to oxygen (path b) or the hydrogen attached to the α-C-atom (path c)? (ii) Is H· eliminated only from (1) or can hydrogen be lost directly from one of the isomerization intermediates of (2), e.g. (4) or (5)? In this communication we answer these questions by means of molecular orbital calculations as well as new labelling experiments.

We have used a modified version of the Gaussian 80 series of programmes.[6] Minima (equilibrium structures) and saddle points (transition states) on the potential energy surface were determined by gradient optimization techniques at the UHF/4-31G level.[7a,b] Zero-point energies were also calculated at this level. Improved energies were obtained by performing single point calculations at the 4-31G optimized geometries with the 6-31G* [7c] and the 6-31G** [7c] basis sets, and by including valence electron correlation at the MP2 and MP3 levels.[7d] The results of the calculations which are most important in the present context are shown in Figure 1.† In agreement with experiment[3] (2) is found to be the most stable

$C_2H_4O^{\cdot+}$ species and to lie 15.2 kcal/mol‡ below (1). The carbene ion radical (5) is only 2.8 kcal/mol higher in energy than (1).§
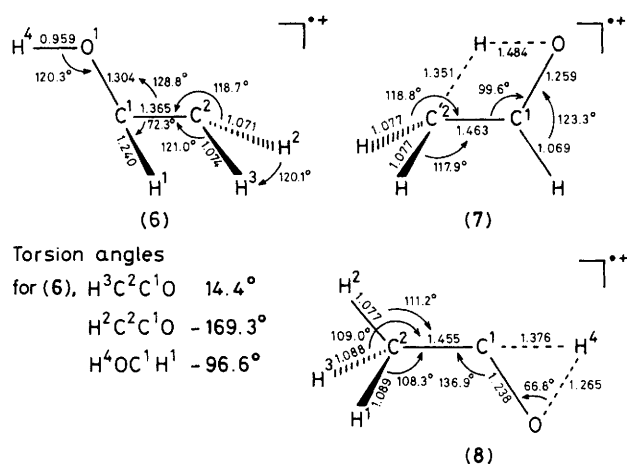
The rearrangement processes of (2) (Scheme 2) require relatively high activation energies, but the direct dissociation processes are even higher in energy. The rearrangement (2) → (5) via transition state (6) (path c) requires the lowest energy (51.3 kcal/mol; MP3/6-31G*). The alternative [1,3]hydrogen shift via (7) (path a) is higher in energy by 4.7 kcal/mol. The inclusion of both polarization functions on the migrating hydrogen and correlation energy are essential for an accurate evaluation of the difference in energy between (7) and (6), which is of crucial importance for the reaction path {i.e., $\Delta E[(7) - (6)]$, kcal/mol, 11.6 (6-31G*), 14.1 (6-31G**), 4.7 (MP3/6-31G*), 7.2 (estimated at MP3/6-31G**) }. We were unable to locate a transition state for the rearrangement (2) → (4) (path b). Furthermore, (4) is not a minimum on the potential energy surface, and we presume that the energy of path b is higher than that of either path a or c.

The ion (5) can either rearrange to (1) (path c) or dissociate directly to $CH_3CO^+ + H\cdot$. This latter alternative was overlooked previously. The activation energy for the (5) → (1) rearrangement via transition state (8) is 39.2 kcal/mol (MP3/6-31G*). The dissociation process of (5) to $CH_3CO^+ + H\cdot$, via (9), requires a slightly lower energy, i.e., 30.0 kcal/mol. Thus, the calculations predict that (2) first rearranges to (5), most of which eventually dissociates directly to $CH_3CO^+ + H\cdot$. Only a minor fraction of (5) may rearrange further to (1) prior to dissociation. For (1) it has already

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† Unless otherwise stated all relative energies are given at the MP3/6-31G*//4-31G level and include zero point energies. The MP3/6-31G** values are estimated by assuming additivity of the effects of correlation energy and polarization functions. See for example: R. H. Nobes, W. J. Bouma, and L. Radom, *Chem. Phys. Lett.*, 1982, **89**, 497.

‡ 1 cal = 4.184 J.

§ This is in reasonable agreement with the recent experimental estimate that (5), a minimum on the potential surface of $C_2H_4O^{\cdot+}$,[5,8] is higher in energy by 25.7 ± 5 kcal/mol than (2).[8]

(6)

(7)

Torsion angles

for (6), $H^3C^2C^1O$ 14.4°

$H^2C^2C^1O$ -169.3°

$H^4OC^1H^1$ -96.6°

(8)

been shown experimentally[3b] that direct dissociation to (3) via (10) is the energetically preferred pathway. Our calculations (Figure 1) support this conclusion. Note that there is neither theoretical nor experimental evidence for a [1,3]-hydrogen migration (2) → (1) (path a), preceding hydrogen loss. The latter is substantiated by the investigation of the unimolecular dissociation of the deuteriated enol ions (2a), (2b), and (2c), respectively, which were generated from appropriately labelled cyclobutanols via dissociative ionization.[4] The ions (2a) and (2c) specifically eliminate D·, and (2b) undergoes only H· loss. These findings certainly rule out path a as well as direct dissociation of (2).¶

(2a)

(2b)

(2c)
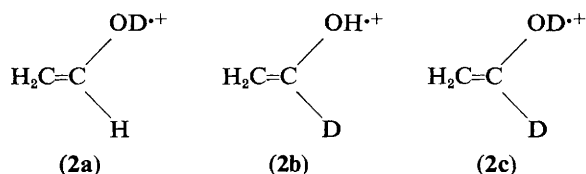
¶ It should be mentioned, however, that collisional activation of (2) opens up an additional decomposition channel, which we believe corresponds to the direct cleavage of the hydrogen-C(α) bond. The results, that (2a) upon C.A. eliminates 9% H and 91% D, (2b) 98% H and 2% D, and (2c) 100% D, respectively, are in good agreement with such an interpretation.

Finally, we note that because the barriers to both dissociation and rearrangement of (5) are relatively high, this key intermediate in the gas phase chemistry of the $C_2H_4O^{·+}$ ions may be observed under appropriate conditions. After completion of this theoretical work, (5) was indeed observed experimentally.[5a,8]

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