The [\( \text{CH}_2 = \text{CHOH}/\text{H}_2\text{O} \)]\(^{+} \) System: a Theoretical Study of Distonic Ions, Hydrogen-bridged Ions and Ion–Dipole Complexes

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Several isomeric forms of the vinyl alcohol/water radical cation have been investigated by high-level ab initio molecular orbital theory calculations, including electron correlation effects. Of the ions considered here, the anti form of the \(-\text{O} \cdots \text{H} \cdots \text{O} \)-bridged complex is calculated to be the lowest in energy, having a stabilization energy of 100 kJ mol\(^{-1}\) with respect to the dissociation products [\( \text{CH}_2\text{CHOH} \)]\(^{+}\) and \( \text{H}_2\text{O} \). Although the isomeric ions may formally be represented as distonic ions, hydrogen-bridged ions and ion–dipole complexes, the only significant barrier separating the isomers appears to be the anti\(\leftrightarrow\)syn isomerization barrier. However, in the \(-\text{O} \cdots \text{H} \cdots \text{O} \)-bridged complex this barrier is found to be considerably lowered relative to the anti\(\leftrightarrow\)syn isomerization barrier for the free vinyl alcohol radical cation.

INTRODUCTION

The combination of mass spectrometric measurements with the results of ab initio calculations has led to the identification and energies of many stable organic cations of unconventional structure. For example the ylidion, [CH\(_2\)OH\(_2\)]\(^{+}\), an isomer of ionized methanol, and a wide variety of analogues [CH\(_2\)XH\(_2\)]\(^{+}\), (X=NH\(_2\), F, Cl, Br, SH, PH\(_3\)) have been characterized by both theory and experiment as stable species in the gas phase.\(^{1-8}\) Theoretical calculations\(^{9,10}\) show that their neutral ylide counterparts are far less stable, in agreement with recent experimental observations using the technique of neutralization reionization mass spectrometry (NRMS).\(^{11,12}\)

Closely related are the [C\(_4\)H\(_6\)O\(_2\)]\(^{+}\) distonic ions, of which the isomer [CH\(_2\)CH\(_2\)OH\(_2\)]\(^{+}\) has been investigated in considerable detail.\(^{3,13}\) It is the most stable C\(_4\)H\(_6\)O\(_2\)]\(^{+}\) isomer, having a stabilization energy of \(~89\) kJ mol\(^{-1}\) relative to its dissociation products [C\(_4\)H\(_6\)]\(^{+}\) + \( \text{H}_2\text{O} \). Its properties, as revealed by theory, can best be described in terms of ion–dipole interactions between ionized ethene and water.\(^{3,6}\) To move the water molecule from one carbon atom to the other requires only 7 kJ mol\(^{-1}\). Well below the dissociation limit, interconversion with a \(-\text{C} \cdots \text{H} \cdots \text{O} \)-bridged species, [CH\(_2\)=CH\(_2\)\cdots H\cdots OH\(_3\)]\(^{+}\), which only occupies a very shallow well, becomes possible. Similar behaviour is observed for the [CH\(_2\)\cdots C=O/\text{H}_2\text{O}]\(^{+}\) system.\(^{4}\)

In contrast, hydrogen-bridged radical cations having an \(-\text{O} \cdots \text{H} \cdots \text{O} \)-bridge are much more stable.\(^{5,6}\) For example, it was shown in a recent combined theoretical and experimental study\(^{14}\) that the hydrogen-bridged ions

\[
\text{[CH}_2\text{O(H)} \cdots \text{H} \cdots \text{O} \equiv \text{CH}_2\text{]}\(^{+}\),
\]

\[
\text{[CH}_2\equiv \text{O(H)} \cdots \text{H} \cdots \text{O} \equiv \text{CH}_2\text{]}\(^{+}\)
\]

and

\[
\text{[CH}_3\text{O} \cdots \text{H} \cdots \text{O} \equiv \text{CH}_2\text{]}\(^{+}\)
\]

are considerably more stable than the conventional isomer [CH\(_2\)OHCH\(_2\)OH\(_2\)]\(^{+}\), by 92, 54 and 33 kJ mol\(^{-1}\), respectively.

In 1984 we reported an experimental study on the structure of the [C\(_4\)H\(_6\)O\(_2\)]\(^{+}\) ion generated by dissociative ionization of butan-1,4-diol.\(^{15}\) The dissociation characteristics and the derived heat of formation (\(\Delta H_f^\circ\) \(~460\) kJ mol\(^{-1}\)) of this ion are only compatible with a complex of water with ionized vinyl alcohol. Such an ion can formally be represented as (i) an \(-\text{O} \cdots \text{H} \cdots \text{O} \)-hydrogen-bridged species,

\[
\text{[H}_2\text{C} \equiv \text{CH} \equiv \text{O} \cdots \text{H} \cdots \text{OH}_2\text{]}\(^{+}\), 1,
\]

(ii) the distonic ions

\[
\text{[H}_2\text{O} \equiv \text{CH}_2 \equiv \text{CHOH}\text{]}\(^{+}\), 8,
\]

and

\[
\text{[CH}_2\equiv \text{CH(OH)} \equiv \text{OH}_2\text{]}\(^{+}\), 3,
\]

and (iii) \(-\text{C} \cdots \text{H} \cdots \text{O} \)-hydrogen-bridged species like

\[
\text{[CH}_2\equiv \text{C(OH)} \equiv \text{H} \cdots \text{OH}_2\text{]}\(^{+}\), 2,
\]

and

\[
\text{[H}_2\text{O} \cdots \text{H} \equiv \text{CH} \equiv \text{CHOH}\text{]}\(^{+}\), 6.
\]

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These and other possible ion structures are presented in Fig. 1.

Experiments do not permit a distinction to be made between these species: all of the structures in Fig. 1 can easily account for the observation that the metastable ion (MI) and collisional activation (CA) mass spectra are dominated by the loss of H₂O (specifically D₂O with 1,4-butadiol (OD) as the precursor molecule) producing [CH₂=CHOH]⁺ with an associated small kinetic energy release. It was therefore considered necessary to turn to ab initio molecular orbital theory calculations to settle which of the eight structures are stable ions and how they may interconvert. A preliminary theoretical study has already indicated that an ion of type (i) (isomer 1 in Fig. 1) is stable. However, the calculations were limited to this isomer, i.e., the syn and anti form (see Fig. 2) and the barrier between them, and correlation effects were not included.

In this paper results of extensive ab initio calculations are presented, including correlation effects, on the relative energies of all the ions shown in Fig. 1, and the barriers for their interconversion.

THEORETICAL METHODS AND CALCULATIONS

Standard LCAO-MO-SCF calculations were performed using the program GAMESS, employing restricted Hartree Fock (RHF) and unrestricted Hartree Fock (UHF) procedures. The geometries of the isomers were determined using analytical gradient optimization procedures. Standard 4-31G and 6-31G** basis sets were used.

The geometry of the isomeric [CH₂CHOH/H₂O]⁺ structures, displayed in Fig. 1, plus some transition states were optimized at the SCF/4-31G level of accuracy and used for single point calculations performed at the SCF/6-31G** level. The geometry optimizations were carried out in the symmetries given in Table 1, and the force constant matrices for all stationary points were checked to have the correct number of negative eigenvalues (0 for equilibrium structures and 1 for transition states). For some isomers, i.e., 4, 5, 7, and 8, certain constraints were adopted which will be discussed later. It may be argued that it is desirable to include polarization functions directly in the geometry optimization (a UHF/6-31G**//6-31G** calculation), but to perform such calculations for all of the above structures is beyond our computational means and, moreover, was found to give only a modest improvement in the accuracy of the relative energies; from the UHF/6-31G**//6-31G** total energies for ion 1 (−228.68568 u) and its dissociation products [CH₂=CHOH]⁺ (−152.62138 u) and H₂O (−76.02361 u) a stabilization energy of 107 kJ mol⁻¹ is obtained. This result is satisfactorily close to that derived from our adopted single point UHF/6-31G**//4-31G computational procedure, 103 kJ mol⁻¹ (see Table 1). UHF/6-31G**//4-31G total energies, the difference being 4 kJ mol⁻¹ (correction a, see below). Single and double excitation configuration interaction (SDCI) calculations were performed for the SCF/4-31G optimized geometries using the ATOMOL package and the DIRECT-CI programs, with the 4-31G basis set. The CI results were size consistency corrected, using the formula derived by Pople:

$$ E_{	ext{Pople}} = E_{	ext{SCF}} + E_{	ext{corr}} $$

$$ \times \left(\frac{n^2 + 2n \tan^2 \theta}{n^2} \right)^{1/2} - \frac{1}{2} \left(\sec 2\theta - 1\right) $$

where $E_{\text{corr}}$ represents the SDCI correlation energy $E_{\text{corr}} = E_{\text{CI}} - E_{\text{SCF}}$, $\theta$ is defined through $c_{60} = \cos \theta$, $c_{60}$ being the coefficient of the SCF reference configuration (RHF/4-31G results in Table 1) and $n$ the number of correlated electrons ($n = 25$ in our calculations since the inner-shell orbitals were frozen). The results are shown in Table 1.

In order to check the size consistency correction in the Pople procedure, Eqn (1), a 'supermolecule' calculation was performed on isomer 1. To simulate a non-interacting system, the H⋯O distance between the vinyl alcohol ion and the water molecule was
increased to 50 Å, and then an SDCI calculation was performed. The total energy thus obtained (Table 1, [CH₃CHOH][⁺] + H₂O (50 Å), SDCI/4-31G(Pople)) is -228.71937 u. The final result, -228.71928 u, was obtained by accounting for an ion-dipole interaction of -0.00009 u (from γ₂/q₂, with q = 1 u, r = 94.5 Å (50 Å) and μ = 0.783 u from an SDCI/4-31G/RHF/4-31G calculation on H₂O). It differs by only ~4 kJ mol⁻¹ (correction b, see below) from the SDCI/4-31G(Pople) result (Table 1) of the dissociation products [CH₃CHOH][⁺] and H₂O. When the size consistency correction of Pople is not applied, a size consistency error of 52 kJ mol⁻¹ is obtained (SDCI/4-31G results (Table 1)), thus the Pople formula corrects for the size consistency error by more than 92%.

The best relative energies from this work, denoted as E_rel values, were obtained using the formula

\[ \Delta E_{\text{rel}}/6-31G^* \approx \Delta E_{\text{ladder}}/4-31G \]

\[ + \Delta E(\text{UHF}/6-31G**) - \Delta E(\text{UHF}/4-31G) \]  

(2)

with the addition of a contribution for the zero point vibrational energy (ZPVE). The relative energies calculated with the above additivity scheme (Eqn (2)) are given in Table 1 and are referred to in the text, using the most stable isomer, I, as the anchor point. Such additivity schemes are very useful when the size of the system precludes CI calculations with polarized basis sets. They have been used frequently, 2n,15a-c and have been tested extensively. 15a-d To check the validity of the additivity approximation used in this paper (Eqn (2)), an SDCI calculation with the 6-31G** basis set was performed for isomer I. The result (see Table 2; E_rel, 106 kJ mol⁻¹, is satisfactorily close to the additivity result, 100 kJ mol⁻¹ (see Table 1, E_rel) the difference being ~6 kJ mol⁻¹ (correction c). Similar results were found for the molecular ions of ethylene glycol 15a and glycol aldehyde. 5b

Harmonic vibrational frequencies have been calculated at the SCF level with the 4-31G basis set. These were used to calculate the ZPVE corrections. Since HF calculations are known 16 to overestimate vibrational energy frequencies by ~10%, the ZPVE contributions to the relative energies have been obtained by scaling the calculated HF/4-31G ZPVEs by a factor of 0.9.

<table>
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<th>SDCI/6-31G**</th>
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<tr>
<td>[CH₃CHOH][⁺] (anti)</td>
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<td>-152.53021</td>
<td>-152.61255</td>
<td>-152.01562</td>
<td>-153.02536</td>
<td>106</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>-152.57756</td>
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* See text (correction c).

Table 2. Calculated total energies (Hartrees) and relative energy (kJ mol⁻¹) of isomer 1 and its dissociation products [CH₃CHOH][⁺] + H₂O, based on UHF/4-31G optimized structures

See text (correction c).
Figure 2. 'Anti' and 'syn' conformations in the vinyl alcohol moiety of \([\text{CH}_2=\text{CHOH}/\text{H}_2\text{O}]^{\pm}\) isomers.

All structure parameters were UHF/4-31G optimized, distances are given in ångströms and angles in degrees; those in parentheses in the optimized structure of isomer 1 denote UHF/6-31G** optimized values. All isomers denoted with a prime have the vinyl alcohol hydroxyl group in the 'syn' conformation, all other isomers have this hydroxyl group in the 'anti' conformation (see Fig. 2).

RESULTS AND DISCUSSION

As can be seen from the results given in Table 1, the minimum of the \([\text{CH}_2=\text{CHOH}/\text{H}_2\text{O}]^{\pm}\) potential energy surface is formed by isomer 1, i.e. the anti form of the \(\text{CH}_2=\text{CH}^+\cdot\cdot\cdot\text{OH}^-\cdot\cdot\cdot\text{H}^+\cdot\cdot\cdot\text{OH}^-\) bridged radical cation \([\text{CH}_2=\text{CH}\cdot\cdot\cdot\text{OH}^-\cdot\cdot\cdot\text{H}^+\cdot\cdot\cdot\text{OH}^-]^{\pm}\). The \(\text{C}^+\cdot\cdot\cdot\text{H}^+\cdot\cdot\cdot\text{O}^-\) bridged ions (2 and 6), the pi-bonded species (4 and 5) and the distonic ion 3, have closely similar relative energies and are all less stable than 1. It is proposed that these species are bound mainly by interactions between

the ion \([\text{CH}_2=\text{CHOH}]^{\pm}\) and the \(\text{H}_2\text{O}\) dipole. The cyclic ion 7 and the distonic ion 8 have relative energies which indicate that these species are not stable towards dissociation into \([\text{CH}_2=\text{CHOH}]^{\pm} + \text{H}_2\text{O}\).

The overall picture which emerges from the consideration of the interconversion barriers among the various stable isomers is shown in Fig. 3. The main features of this surface are that all of the stable isomeric ions can freely interconvert below the dissociation limit, but the syn-anti conversion of a given ion (e.g. 2 \(\leftrightarrow\) 6) cannot occur directly. The only isomers which have a facile syn \(\leftrightarrow\) anti conversion are the \(-\text{O}^+\cdot\cdot\cdot\text{H}^+\cdot\cdot\cdot\text{O}^-\) hydrogen bridged species 1 and 1', and communication of an ion in the 'syn channel' with one in the 'anti channel' only occurs via TS1'. In the following sections on the individual ions the properties of the surface will be discussed in more detail.

The \(-\text{O}^+\cdot\cdot\cdot\text{H}^+\cdot\cdot\cdot\text{O}^-\) hydrogen bridged ion 1 and 1' and their transition state TS1'.

Of the structures shown in Fig. 1, the \(-\text{O}^+\cdot\cdot\cdot\text{H}^+\cdot\cdot\cdot\text{O}^-\) hydrogen-bridged isomer,

\([\text{CH}_2=\text{CHOH}\cdot\cdot\cdot\text{H}^+\cdot\cdot\cdot\text{OH}^-]^{\pm}, 1,\)

was found to be the species of lowest energy. Using the additivity scheme, Eqn (2), ion 1 is calculated to have a stabilization energy of 100 kJ mol\(^{-1}\) towards dissociation into \([\text{CH}_2=\text{CHOH}]^{\pm} + \text{H}_2\text{O}\), a value close to the previous SCF result.\(^6\) The geometries of the syn and anti conformations of this ion, 1' and 1, respectively, and the transition state TS1' for their interconversion are shown below.
The results in Table 1 show that the anti isomer is the more stable by 9 kJ mol\(^{-1}\), and the barrier to its interconversion, \(T_{S1}'\), lies 55 kJ mol\(^{-1}\) above I.

Combining all corrections (i.e., corrections a, b, and c discussed in the previous section) and including the basis set superposition error correction (BSSE) calculated in Ref. 6b, \(-5\) kJ mol\(^{-1}\), yields our best value for the stabilization energy of isomer I, which, assuming that all those corrections are additive, is \(100 + 4 - 4 + 6 - 5 = 101\) kJ mol\(^{-1}\).

Using this stabilization energy and experimental values for the heat of formation, \(\Delta H_f^{\text{H}_2\text{O}}\) \(\text{CH}_3\text{CHOH}^+ = 757\) kJ mol\(^{-1}\) and \(\Delta H_f^{\text{H}_2\text{O}}\) of ion I' = 414 kJ mol\(^{-1}\). The result is to be compared with our experimentally derived upper limit, \(\leq 460\) kJ mol\(^{-1}\), and is in excellent agreement with an empirical relationship between the heats of formation of Larson and McMahon for proton-bound dimers.\(^{19}\) \(424\) kJ mol\(^{-1}\) (using \(\Delta H_f^{\text{H}_2\text{O}}\) \(\text{CH}_3\text{CHOH}^+ = 0\) kJ mol\(^{-1}\)), \(\Delta H_f^{\text{H}_2\text{O}}\) \(\text{H}_2\text{O} = -242\) kJ mol\(^{-1}\),\(^{18}\) the derived \(\Delta H_f^{\text{H}_2\text{O}}\) of ion I' = 414 kJ mol\(^{-1}\). This is to be compared with our experimentally derived upper limit, \(\leq 460\) kJ mol\(^{-1}\), and is in excellent agreement with the empirical relationship between the heats of formation of Larson and McMahon for proton-bound dimers.\(^{19}\) \(424\) kJ mol\(^{-1}\) (using \(\Delta H_f^{\text{H}_2\text{O}}\) \(\text{CH}_3\text{CHOH}^+ = 0\) kJ mol\(^{-1}\)), \(\Delta H_f^{\text{H}_2\text{O}}\) \(\text{H}_2\text{O} = -242\) kJ mol\(^{-1}\),\(^{18}\) the derived \(\Delta H_f^{\text{H}_2\text{O}}\) of ion I' = 414 kJ mol\(^{-1}\).

As stated above, the syn conformation of isomer I, I' (see Fig. 2) is less stable than the anti form by 9 kJ mol\(^{-1}\). The transition state between them can be achieved via either a rotation or an inversion \(^{22}\) of the hydroxyl group with respect to the CO bond as shown in Scheme 1.

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**Diagram:**

- **Figure 3:** Schematic potential energy profile of the \([\text{CH}_2=\text{CHOH/H}_2\text{O}]^+\)' system showing the interconversion pathways among the various syn and anti isomers, interconversion and dissociation of \([\text{CH}_2=\text{CHOH/H}_2\text{O}]^+\) isomers. Relative energies \(\Delta E/\text{ kcal mol}^{-1}\) (see Table 1).

- **Figure 4:** Reaction profile of the relative energy showing the effect of varying the position of the hydrogen atom (with fixed optimized O–O distances) in \([\text{CH}_2=\text{CHOH/H}_2\text{O}]^+\), isomer 1. (a) \(\Delta E_{\text{rel}}/\text{ kcal mol}^{-1}\) relative energies with \(\text{HUF/4-31G}^{\text{B}}\) optimized O–O distances. (b) \(\Delta E_{\text{rel}}/\text{ kcal mol}^{-1}\) relative energies with \(\text{HUF/6-31G}^{\text{B}}\) optimized O–O distances (1 kcal = 4.184 kJ).

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Earlier work at the SCF/4-31G level\(^6\) showed the inversion to be less energy-dissipating and gave a barrier of only 9 kJ mol\(^{-1}\). The present calculations which include correlation and polarization effects, put the barrier for interconversion via inversion at a much higher level, \(T_{S1}'\) being 55 kJ mol\(^{-1}\) above I. This increase in barrier height is mainly due to the effect of the polarization functions, as can be seen from a comparison of the \(\text{HUF/4-31G}\) and \(\text{HUF/6-31G}^{\text{B}}\) relative energies for \(T_{S1}'\) in Table 1 and also from the reaction profiles shown in Fig. 4. Nevertheless, interconversion via inversion appeared to remain energetically more favourable than via rotation. In ionized vinyl alcohol itself, analogous to the results of Cremer et al.\(^{22}\) for the XCH\(=\text{CHOH(+)}\) system (X=H, CH\(_3\), NH\(_2\), OH, OH\(_2\)),
CN, etc.), the syn ↔ anti conversion was computed to proceed via rotation of the hydroxyl group (Table 2), saddle (inv) vs. saddle (rot), but the associated barrier, 92 kJ mol⁻¹, is much higher than that for inversion in the hydrogen-bridged ions I and 1'.

The rationale for the decreased barrier for hydroxyl inversion in the [CH₃=CHOH/H₂O]⁺¹ complex is that the bridging H atom can easily move towards the water molecule, as illustrated in Fig. 4, where it can be seen that the potential curves for this motion are relatively flat. This is to be contrasted with the far more energy-demanding extension of the O−H bond in the free [CH₃CHOH]⁺¹ ion.

The result of the above is to reduce the sp² or p-system distortion necessary to achieve TS₁'/. Note that the optimized geometry of this transition state has a long bond between the bridging H and CH₃=CHO−, 1.378 Å, and a short H−OH₂ bond, 1.064 Å. These bond lengths are the opposite of those in the optimized geometries I and 1' shown above.

The C−H−O− hydrogen-bridged ions 2,2' and 6,6' and the transition states TS₂' and TS₆₁'.

Of the isomers 2,2' and 6,6', only the syn isomer 2' and the anti isomer 6 are local minima on the potential energy surface. Their anti and syn conformations, 2 and 6', respectively, are unstable and collapse to 1 and 1', respectively; 2' and 6 are calculated to lie 41 and 42 kJ mol⁻¹, respectively, below the product energy. These stabilization energies compare well with the stabilization energy of the C−H−O− bridged complex in the [C₂H₅/H₂O] system, viz. 43 kJ mol⁻¹. The C−H−O− bond distances are also similar, 2.941 Å in [CH₃=CH−H−OH₂]⁺² with 2.926 Å for 2' and 2.931 Å for 6. The similarity between these three ions lies in their being bound by ion–dipole forces with only a small additional H-bridge stabilization (~9 kJ mol⁻¹). Note also that their geometry shows the water dipole directed towards the centre of the positive charge, which was found to be largely localized at the hydroxyl bearing C-atom (from a Mulliken population analysis).

It should be emphasized that 1 and 1' are more stable than the typical ion–dipole complexes referred to above. This arises from the additional H-bond stabilization to oxygen, rather than to carbon.

The direct conversion of the syn isomer 2' into the (most stable) anti isomer 1 (TS₂'/) and the similar conversion of the anti isomer 6 into the syn isomer 1' (TS₆₁') is not feasible, because the height of these barriers lies above that computed for dissociation (see Table 1). These two transition states each lie ~95 kJ mol⁻¹ above the starting isomers, an energy closely similar to that required for the anti ↔ syn conversion in the isolated [CH₃=CHOH]⁺¹ ion. Thus the high energy requirement for the direct syn ↔ anti conversions 2' ↔ 1 and 6 ↔ 1' appears to be associated with the energy required for OH rotation in the [CH₃=CHOH]⁺¹ moiety of these ions.

However, the conversions 2' ↔ 1 and 6 ↔ 1' readily occur at energies far below the dissociation limit (see Table 1), but via the indirect routes 2' → 3' → 4' → 5' → 6 → 1' → 1 and 6 → 5 → 4 → 3 → 2 → 1 → 1', i.e. via a route in which the syn–anti conversion only occurs in the C−H−O− hydrogen-bridged ions. This is depicted in Fig. 3, where ions in
the 'syn channel' can only communicate with those in the 'anti channel' via TS1'. As will be discussed below, no significant barrier is expected for interconversion of -C⋯H⋯O− bridged ions and distonic ions having the same (syn-anti) conformation (i.e. 2′⋯3′, 6⋯5, etc.). This is because inversion and rotation of the -C⋯H⋯O− bond requires only a small energy, as can be seen from Fig. 5 for the hydrogen-bridged radical cation \([\text{CH}_2\text{CH}⋯\text{H}⋯\text{OH}_2]^+\)\(^\text{36}\). (A similar result was also found for the -C⋯H⋯O− hydrogen-bridged form of the [ketene/water]\(^+\) system.\(^\text{34}\).

The distonic ions 3,3′ and the pi-complexes ion 4,4′ and 5,5′

The distonic isomers are all stable towards dissociation into \([\text{CH}_2\text{CH}⋯\text{CHOH}]^+ + \text{H}_2\text{O}\); their stabilization energies are similar to those found for the -C⋯H⋯O− bridged species 2 and 6: 43, 47 and 43 kJ mol\(^{-1}\), respectively (see Table 1). The relative energy of 3 was explicitly calculated (Table 1); that of its syn isomer 3′ was estimated to be similar—see the results for the syn and anti forms of \([\text{CH}_2\text{CH}⋯\text{CHOH}]^+\) in Table 2. The geometries of the related isomers 4 and 5 were optimized using the constraints shown in the above structures. It appears that their relative energies (Table 1) are very close to that of the true minimum 3, indicating a flat potential energy surface in this region. Although it may be questioned whether the computational procedure used to calculate ZPVE values is reliable for these constrained structures, the use of only Eqn (2) indicates that the potential energy surface around isomer 3 is indeed very flat. In each species the \text{H}_2\text{O} dipole is situated at 2.4–2.5 Å from the centre of charge of the \([\text{CH}_2\text{CH}⋯\text{CHOH}]^+\) ion (see the optimized geometries above, only the anti conformations are given) and we conclude that these isomers are again mainly bound by ion-dipole forces, albeit with shorter C⋯H⋯O distances than in 2 and 6, but again with

![Figure 5. Reaction profiles showing the effect of inversion (c) and rotation (d) of the -C⋯H⋯O bond on the relative energy in the hydrogen-bridged radical cation \([\text{CH}_2\text{CH}⋯\text{H}⋯\text{OH}_2]^+\). The H\(_2\)O dipole pointing towards the positive centre at the hydroxyl-bearing C-atom (from the Mulliken population analysis).\(^\text{6b}\).

These results indicate that far below the dissociation limit, isomers of the same conformation (syn or anti) can easily interconvert and that the system behaves in a manner analogous to that for the ion-dipole species \([\text{CH}_2\text{CH}⋯\text{O}/\text{H}_2\text{O}]^+\)\(^\text{46}\) and \([\text{CH}_2\text{CH}_2\text{H}_2\text{O}]^+\)\(^\text{36}\).

The cyclic ion 7 and the distonic ions 8 and 8′

Finally we have computed the relative energies of the cyclic ion 7 and the distonic ion 8, whose geometry was
obtained by an out of plane rotation of H₂O in 7, keeping fixed the OCCO dihedral angle. As seen in Table 1, both ions are expected not to be stable because their calculated energies lie above the dissociation limit. This is probably also true for 8', which was not further investigated. When structure 8 is fully optimized it appears to collapse into the local minimum 5, i.e. the original structure, having a relatively short (covalent) bond between the H₂O oxygen and the vinyl alcohol moiety (1.531 Å), becoming a typical ion-dipole species with a significantly increased intermolecular distance (2.9 Å). Thus, in contrast to the [ethene/H₂O]⁺ system where the global minimum is formed by the distonic ion [CH₂CH₂—OH]⁺ with a relatively small C—O distance (1.65 Å)²⁻ the [vinyl alcohol/H₂O]⁺ system only contains a stable distonic species with a corresponding longer bond. This result pertains to the SCF/6-31G* level only; at the other levels of theory the ions are computed to be marginally stable towards dissociation. The instabilities of 7 and 8 as computed by our adopted procedure could be incorrect owing to a basis set deficiency between the SCF/4-31G optimized structure and the single point calculation at the SCF/6-31G* level. However, we do not expect that the inclusion of polarization functions in the geometry optimization (a SCF/6-31G*/6-31G* calculation, see previous section) will result in a more than nominal stability for these species.

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