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Formaldehyde mediated proton-transport catalysis in the ketene–water radical cation $CH_2{=}C({=}O)OH_2^{\bullet+}$

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Dedicated to Professor Diethard K. Böhme on the occasion of his 65th birthday.

Abstract

Previous studies have shown that the solitary ketene–water ion $CH_2{=}C({=}O)OH_2^{\bullet+}$ (**1**) does not isomerize into $CH_2{=}C(OH)_2^{\bullet+}$ (**2**), its more stable hydrogen shift isomer. Tandem mass spectrometry based collision experiments reveal that this isomerization does take place in the $CH_2{=}O$ loss from *low-energy* 1,3-dihydroxyacetone ions $(HOCH_2)_2C{=}O^{\bullet+}$.

A mechanistic analysis using the CBS-QB3 model chemistry shows that such molecular ions rearrange into hydrogen-bridged radical cations $[CH_2C({=}O)O(H){-}H\cdots OCH_2]^{\bullet+}$ in which the CH_2O molecule catalyzes the transformation **1** → **2** prior to dissociation. The barrier for the unassisted reaction, 29 kcal mol^{-1}, is reduced to a mere 0.6 kcal mol^{-1} for the catalysed transformation. Formaldehyde is an efficient catalyst because its proton affinity meets the criterion for facile proton-transport catalysis.

Keywords: Proton-transport catalysis; Ketene–water ion; 1,3-Dihydroxyacetone; CBS-QB3; Hydrogen-bridged radical cation

1. Introduction

A very recent review elegantly demonstrates that the application of mass spectrometric techniques to the study of elementary ion reactions has led to remarkable progress in the characterization of detailed aspects of the kinetics, thermodynamics, and mechanisms of *molecular* transformations catalyzed by *ions* in the gas-phase [1].

This active field of research has greatly benefited from the selected-ion flow tube (SIFT) studies of Böhme and his research group [1]. This is also true for the related area of research which studies *ionic* transformations catalyzed by *molecules* in the gas-phase. As pointed out in Böhme's early review on this topic [2], a pair of solitary ionic isomers whose interconversion barrier is prohibitively high may be induced to interconvert via proton transfer in an encounter complex with a neutral molecule having the correct proton affinity (PA). This process is commonly called proton-transport catalysis (PTC). As a result the higher energy isomer may be transformed into its thermodynamically more stable counterpart.

For example [3], a large 1,2-H shift barrier prevents the conversion of ionized hydroxycarbene into ionized formaldehyde: $HCOH^{\bullet+} \not\rightarrow CH_2{=}O^{\bullet+}$. The barrier exceeds the energy required for loss of $H^\bullet$ by direct bond cleavage, so even high energy ions will dissociate rather than interconvert. However, when a neutral molecule is allowed to interact with $HCOH^{\bullet+}$ proton-transport catalysis (PTC) may promote its isomerization into the lower energy $CH_2{=}O^{\bullet+}$ isomer. The molecule may act as a base (B) and accept a proton from one site of the $HCOH^{\bullet+}$ substrate, and then donate it back to a different site, as illustrated in Eq. (1):

$$\begin{aligned} HCOH^{\bullet+} + B &\rightarrow HCO{-}H^{\bullet+}\cdots B\,(a) \rightarrow HC{=}O^{\bullet}\cdots HB^{+} \\ &\rightarrow O{=}C(H)^{\bullet}\cdots HB^{+} \rightarrow O{=}C(H){-}H^{\bullet+}\cdots B\,(b) \\ &\rightarrow CH_2{=}O^{\bullet+} + B \qquad (1) \end{aligned}$$

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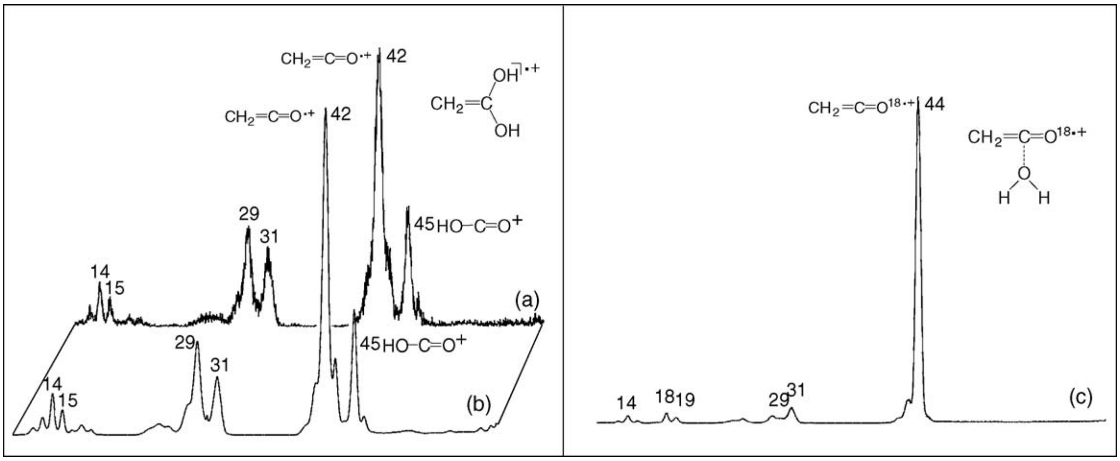

Fig. 1. CID mass spectra of (a) the $C_2H_4O_2^{\bullet+}$ ions generated by loss of $CH_2{=}O$ from metastable 1,3-dihydroxyacetone ions; (b) the enol ion of acetic acid, $CH_2{=}C(OH)_2^{\bullet+}$; (c) the ^{18}O labelled ketene–water ion $CH_2{=}C({=}O^{18})OH_2^{\bullet+}$.

Criteria for successful proton-transport catalysis have been further developed by Radom and Gauld [4]. The most important criterion states that a smooth isomerization for the reaction of Eq. (1) occurs if the PA of the base B lies between the PA of $HCO^{\bullet}$ at O and at C. If PA(B) is too low, proton abstraction will not take place. If PA(B) is too high, the incipient ion BH^+ will not release the proton: dissociation to $HCO^{\bullet} + BH^+$ will ensue instead. As reported recently [5], the criterion can be significantly extended downwards to include bases of lower PA with a concomitant increase of the barrier height.

Several examples of ion–molecule reactions in the gas-phase are now available [6] where interaction of a radical cation with a single, judiciously chosen, “solvent” molecule leads to its transformation into a more stable isomer. Key intermediates in these reactions are hydrogen-bridged radical cations (HBRCs) [7] of the type (a) and (b) in Eq. (1). However, we note that not all such catalyzed transformations involve transport of a proton rather than a hydrogen atom [6c] and also that these transformations may take place in the dissociative ionization of molecules [3].

In the context of studies on proton-transport catalysis, the Böhme group presented intriguing experimental and computational results on the water-catalyzed hydrolysis of the ketene radical cation at the 2004 Trent Conference in Mass Spectrometry [8]. Ketene ions were allowed to react with water in the SIFT mass spectrometer and one aspect of their study dealt with the water catalyzed isomerization of the incipient ketene–water ion, $CH_2{=}C({=}O)OH_2^{\bullet+}$ (**1**), into its thermodynamically more stable isomer $CH_2{=}C(OH)_2^{\bullet+}$ (**2**), the enol ion of ionized acetic acid, $CH_3{-}C({=}O)OH^{\bullet+}$ (**3**).

The criterion for efficient PTC for the transformation $CH_2{=}C({=}O)OH_2^{\bullet+}$ (**1**) → $CH_2{=}C(OH)_2^{\bullet+}$ (**2**) stipulates[1] that the base has a PA in the range of 166–183 kcal mol^{-1} and hence water (PA = 167 kcal mol^{-1}) is a suitable catalyst. The PA of the formaldehyde molecule, 170 kcal mol^{-1} [10b], also satisfies the PTC criterion. Thus it may be expected that formaldehyde can also efficiently catalyse the isomerization.

This information inspired us to re-examine the generation of **1** as the product ion of the dissociative ionization of 1,3-dihydroxyacetone: $(HOCH_2)_2C{=}O^{\bullet+}$ (DHA-**1**) → $CH_2{=}C({=}O)OH_2^{\bullet+}$ (**1**) + $CH_2{=}O$. In 1986 Postma et al. [9] provided experimental and supporting computational evidence that the *source* generated $C_2H_4O_2^{\bullet+}$ ions of this dissociation have the connectivity of ketene–water type ions **1**. The ion undergoes one major unimolecular dissociation, loss of H_2O to yield $CH_2{=}C{=}O^{\bullet+}$. This process is associated with a very small kinetic energy release indicative of a species in which a water molecule is attached to ionized ketene by an ion–dipole bond. Loss of water also wholly dominates the collision induced dissociation (CID) mass spectrum, which is characteristically different from that of any other $C_2H_4O_2^{\bullet+}$ isomer, including $CH_2{=}C(OH)_2^{\bullet+}$ (**2**).

Thus, there is little doubt that the *source* generated *m/z* 60 $C_2H_4O_2^{\bullet+}$ ions from DHA-**1** are (largely) ketene–water type ions **1**.

Appearance energy measurements of the *m/z* 60 ion [9] yielded an apparent heat of formation of 138 kcal mol^{-1} which was interpreted to correspond to the formation of **1** at the thermochemical threshold. This implies that the abundant loss of $CH_2{=}O$ from low-energy ions DHA-**1** – the MI spectrum of DHA-**1** is dominated by a simple Gaussian shaped peak [11] at *m/z* 60 corresponding with a $T_{0.5}$ value of 25 meV – would also yield $C_2H_4O_2^{\bullet+}$ ions of structure **1**.

This proposal could be verified by analyzing the CID mass spectrum of the *m/z* 60 ions generated from *metastable* DHA-**1** ions. Such an experiment could not be performed with the instrumentation of the study of Ref. [9] but our three-sector ZAB-R magnetic deflection instrument does have this capability.

The result of this experiment is shown in Fig. 1a. The spectrum is virtually identical with that of enol ions $CH_2{=}C(OH)_2^{\bullet+}$ (**2**), see Fig. 1b. It is incompatible with the formation of the ketene–water isomer $CH_2{=}C({=}O)OH_2^{\bullet+}$ (**1**) whose ^{18}O isotopomer $CH_2{=}C({=}O^{18})OH_2^{\bullet+}$ yields the spectrum of Fig. 1c.

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[1] Using $\Delta_f H$ [$^{\bullet}CH_2COOH$] = −61.6 kcal mol^{-1} [10a], $\Delta_f H$ (**1a**) = 138.5 kcal mol^{-1} (Table 1), $\Delta_f H$ (**2**) = 121.8 kcal mol^{-1} (Table 1).

Table 1
Enthalpies of formation (kcal mol^{-1}) and total energies (Hartree) derived from CBS-QB3 calculations

Isomer	E_{total} (0 K)	$\Delta_f H^\circ_{298}$	Isomer	E_{total} (0 K)	$\Delta_f H^\circ_{298}$
DHA-**1**	−342.75044	92.9	**1a**	−228.38018	138.5
DHA-**2**	−342.73670	102.2	**1b**	−228.38058	138.4
DHA-**3**	−342.74391	98.6	**1c**	−228.34425	160.4
DHA-**4**	−342.75694	89.7	**2**	−228.40494	121.8[a]
DHA-**5**	−342.76572	83.9	**3**	−228.37212	142.5[b]
DHA-**6a**	−342.78428	72.3	**4**	−229.54435	136.7
DHA-**6b**	−342.78676	70.6	TS **1a** → **2**	−228.33042	168.5
DHA-**7**	−342.73078	107.6	TS **1a** → **3**	−228.30139	187.0
TS DHA-**1** → **2**	−342.73165	104.8	TS **2** → **3**	−228.33128	167.8
TS DHA-**2** → **3**	−342.71951	113.0	TS **1a** → **1c**	−228.34001	162.8
TS DHA-**3** → **4**	−342.74307	99.2	TS **1a** → **1b**	−228.38110	137.6
TS DHA-**4** → **5**	−342.75310	91.7	$CH_2{=}C{=}O^{\bullet+}$	−152.02212	210.2[c]
TS DHA-**5** → **6**	−342.76421	84.5	H_2O	−76.33382	−58.3
TS DHA-**2** → **7**	−342.71562	115.7	$CH_2{=}O$	−114.34411	−27.3

[a] Lowest energy conformer; experimental value = 120 kcal mol^{-1} [10c].

[b] Lowest energy conformer; experimental value = 142.5 kcal mol^{-1} [10c].

[c] Experimental value = 210.2 kcal mol^{-1} [10c].

This spectrum shows a specific loss of $H_2{}^{16}O$, confirming that ions **1** do not communicate with ions **2** prior to dissociation.

Thus, the formaldehyde loss from low-energy DHA-**1** ions does *not* yield ketene–water ions **1** but rather enol ions **2**, possibly by a formaldehyde-catalyzed isomerization **1** → **2**. The derived heat of formation of 138 kcal mol^{-1} for the *m/z* 60 product ion generated in the formaldehyde loss (see above) is not compatible with the threshold formation of **2** (122 kcal mol^{-1}, see Table 1) but could result from an energy barrier in the rearrangement.

This intriguing result prompted us to explore the mechanism of the formaldehyde loss from low-energy 1,3-dihydroxyacetone ions using computational chemistry. During the past 5 years we have successfully used the CBS-QB3 method [12] in mechanistic studies of proton-transport catalysis in various organic radical cations [13]. We therefore decided to use this CBS variant, which uses density functional geometries and frequencies in the calculations, as the primary computational tool in probing the mechanism for the formaldehyde elimination from metastable ions DHA-**1**.

It will be shown that proton-transport catalysis indeed accounts for the formation of enol ions **2** in the formaldehyde loss from low-energy 1,3-dihydroxyacetone radical cations.

2. Experimental and theoretical methods

The experiments were performed with the VG Analytical ZAB-R mass spectrometer of BEE geometry (B, magnet; E, electric sector) [14] using an electron ionization source at an accelerating voltage of 8 kV. Metastable ion (MI) mass spectra were recorded in the second field free region (2ffr). The CID mass spectra of the 2ffr metastable peaks were obtained in the 3ffr using O_2 as collision gas (transmittance, $T = 70\%$). The reference CID mass spectrum of the enol ion of acetic acid of Fig. 1b was obtained via the dissociative ionization of butyric acid. The spectrum of Fig. 1c was obtained in the context of a previously reported study of ionized oxalacetic acid: it pertains to the decarbonylation of metastable α-hydroxy(^{18}OH) acrylic acid ions into $CH_2{=}C({=}O^{18})OH_2{}^{\bullet+}$ as indicated in Scheme 3 of Ref. [15]. All spectra were recorded using a PC-based data system developed by Mommers Technologies Inc. (Ottawa).

The 1,3-dihydroxyacetone sample was of research grade (Aldrich) and used without further purification.

The calculations were performed with the CBS-QB3 model chemistry [12] using Gaussian 2003, Rev C.02 [16] and (for selected transition state searches) GAMESS-UK [17]. In this model chemistry the geometries of minima and connecting transition states are obtained from B3LYP density functional theory in combination with the 6-311G(2d,d,p) basis set (also denoted as the CBSB7 basis set). The resulting total energies and enthalpies of formation for minima and connecting transition states (TS) in the 1,3-dihydroxyacetone system of ions are presented in Table 1. Spin contaminations were within an acceptable range (0.76–0.86). Fig. 3 displays the optimized geometries for the principal species. The complete set of computational results is available from the authors upon request.

3. Results and discussion

3.1. The structure and stability of the ketene–water ion and the relationship with its hydrogen shift isomers $CH_2{=}C(OH)_2{}^{\bullet+}$ (**2**) and $CH_3{-}C({=}O)OH^{\bullet+}$ (**3**)

In the early ab initio calculations of Postma et al. [9], the RHF/4-31G level of theory was used to optimize the geometries of various configurations of the ketene–water ion. Our CBS-QB3 calculations agree with their findings that ion **1a** and the hydrogen-bridged radical cation **1b**, whose optimized geometries are shown in Fig. 3, represent the most stable configurations. The two ions have similar energies and our calculations further agree that the barrier for the interconversion **1a**/**1b** is negligible (see Table 1). At internal energies in excess of only a few kcal mol^{-1} above **1a**/**1b**, the water molecule can freely move from carbon to carbon. The sum of the product energies relative to **1a** was calculated to be 15 kcal mol^{-1} [9] which reasonably agrees with our CBS-QB3 result of 13.4 kcal mol^{-1}.

The optimized geometry of **1a** shown in Fig. 3a points to a description of the ion as a (ketene)ion–(water)dipole complex. Using the simple equation for the ion–dipole stabilization energy – SE (kcal mol^{-1}) = 68.8μ/r^2, with μ = dipole moment (D) and r = distance (Å) between the charge and the dipole) – one obtains SE (**1a**) = 27 kcal mol^{-1}, much larger than the CBS-QB3 derived value of 13.4 kcal mol^{-1}. However, the above equation does not account for repulsive effects associated with an ion–dipole interaction. That such a repulsive destabilizing effect operates in **1a** follows from an inspection of the geometries of the ketene ion in **1a** and **1b**, see Fig. 3a. In **1b** the ketene ion has a linear configuration but in **1a** repulsion of the oxygen atoms' lone pairs causes the ion to adopt an energetically less favourable "bent" structure. In a valence bond type of description, structure **1a** suffers from some contribution of the distonic form $^{\bullet}CH_2–C(OH_2^+)=O$, raising the total energy.

Postma et al. [9] further reported that point calculations for other geometries related to H_2O motion about the ends of the ketene ion showed barriers to such motion. One such motion leads to an isomer of the connectivity $H_2O–CH_2=C=O^{\bullet+}$ having an O–C bond length of 2.839 Å, which was calculated to lie ~6 kcal mol^{-1} above **1a**. This structure is probably not a minimum on the PES: when we optimized its geometry with the CBS-QB3 method, a minimum was located which corresponds with the distonic ion $H_2O–CH_2–C=O^{\bullet+}$ (**1c**), having an O–C bond of 1.533 Å (see Fig. 3). This ion is only marginally stable – it lies 22 kcal mol^{-1} higher in energy than **1a** and requires only 2.5 kcal mol^{-1} to rearrange into energy rich ions **1a** which subsequently dissociate – but it does play a role in the mechanism discussed in the next section.

Our computational results, see Table 1, further show that the unassisted isomerization of ions **1a** into the enol of acetic acid ion **2** is prohibitively high: the associated energy barrier of 29 kcal mol^{-1} lies well above the energy required for dissociation by direct bond cleavage into $CH_2=C=O^{\bullet+} + H_2O$. The same holds true for the isomerization **1a** → **3**. Thus solitary ketene–water ions do not communicate with their 1,3-hydrogen shift isomers $CH_2=C(OH)_2^{\bullet+}$ (**2**) and $CH_3–C(=O)OH^{\bullet+}$ (**3**).

3.2. The loss of formaldehyde from low-energy 1,3-dihydroxyacetone ions

We will use the energy diagram of Fig. 2 as a guide in the discussion of our proposed mechanism for the formation of enol ions **2** from metastable 1,3-dihydroxyacetone ions. Starting from ion DHA-**1**, we see that elongation of the $HOCH_2–C(=O)$ bond with the concomitant formation of a new O–H bond may lead to the hydrogen-bridged radical cation DHA-**2** via a low-energy barrier. Ion DHA-**2** then rearranges, via a barrier which is calculated to lie at 113 kcal mol^{-1}, into a ter-body complex, ion DHA-**3**. The height of this barrier is very close to the enthalpy calculated for the dissociation level **1a** + $CH_2=O$, 112 kcal mol^{-1}, and this supports – see Section 1 – our alternative interpretation of the AE measurements of Postma et al. [9], namely that the experimental AE actually corresponds to a barrier, i.e., TS DHA-**2** → **3**.

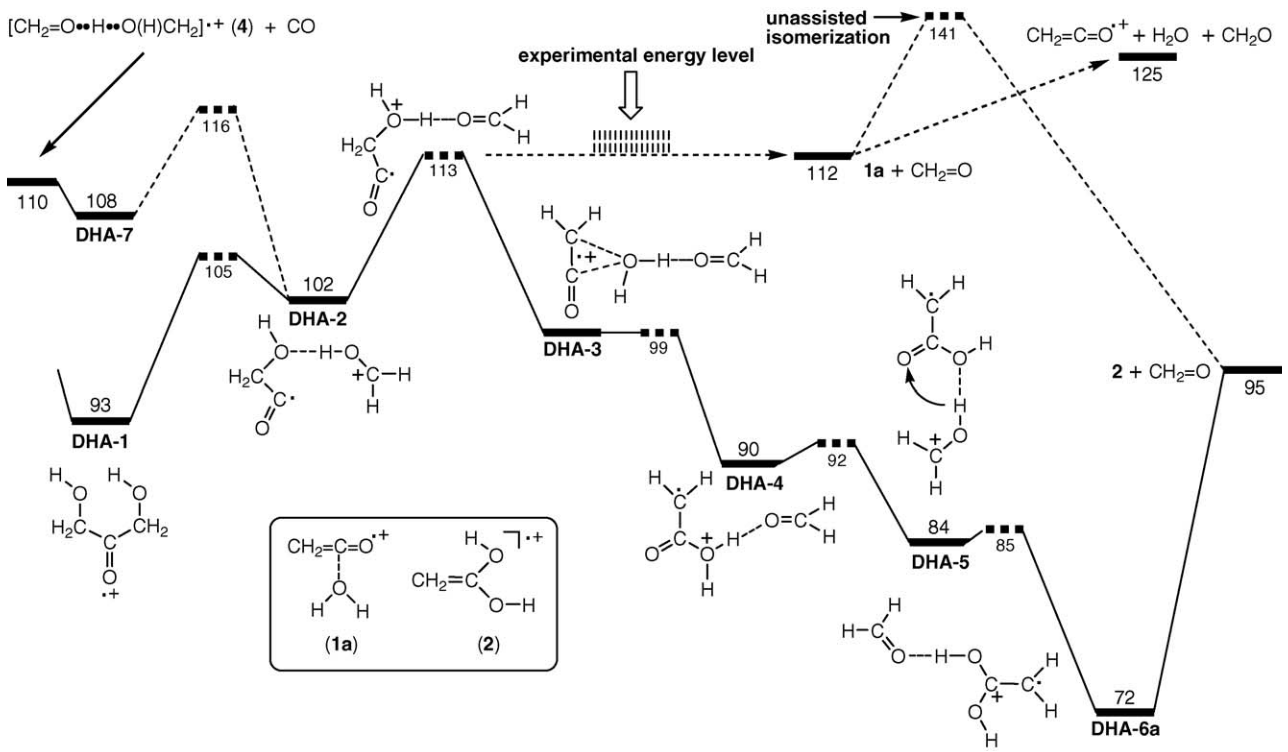

Fig. 2. Energy level diagram derived from CBS-QB3 calculations (298 K values in kcal mol^{-1}) describing the formation of enol ions **2** via loss of $CH_2=O$ from metastable 1,3-dihydroxyacetone ions.

Once ions DHA-**3** have been formed, they may undergo a barrierless rearrangement involving the migration of the $OH_2\cdots O{=}CH_2$ moiety to the carbon atom of the carbonyl group of the ketene part to form HBRC DHA-**4**. A rotation of the $OH_2\cdots O{=}CH_2$ moiety yields its more stable conformer DHA-**5**, via a TS lying only 2 kcal mol^{-1} above DHA-**4**. A formal 1,3-H shift assisted by the $CH_2{=}O$ molecule in DHA-**5**, the proton-transport catalysis step, then yields DHA-**6**, the desired precursor ion for the generation of **2** + $CH_2{=}O$. The TS connecting DHA-**5** and DHA-**6** lies at 85 kcal mol^{-1}, well below the energy requirement for dissociation into **2** + $CH_2{=}O$, at 95 kcal mol^{-1}.

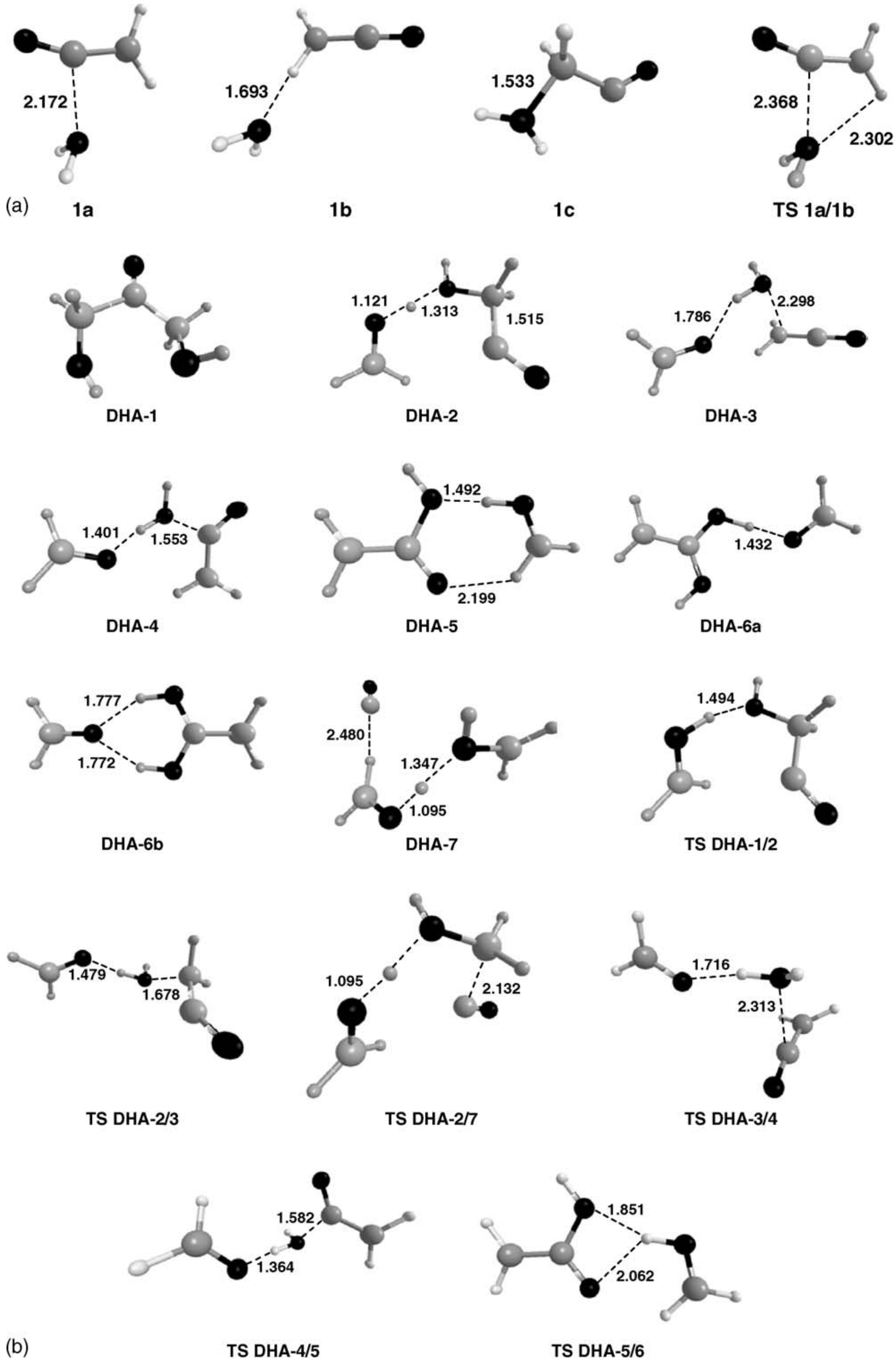

Fig. 3. (a) Optimized geometries (CBSB7 basis set) of stable configurations on the potential energy surface of the ketene–water radical cation (bond lengths in Å); (b) selected optimized geometries (CBSB7 basis set) for stable intermediates and transition states involved in the formaldehyde elimination from ionized 1,3-dihydroxyacetone (DHA-**1**).

It was stated in the Introduction that since formaldehyde fulfils the PA criterion, the transformation should be smooth, i.e., the barrier for proton-transport catalysis should be low. Indeed, as can be seen from Fig. 2 and Table 1, the barrier for the isomerization is reduced from 29 kcal mol^{-1} for the solitary ions to a mere 0.6 kcal mol^{-1} for the formaldehyde assisted transformation showing that formaldehyde is an efficient catalyst.

Loss of formaldehyde by a simple O–H–O=CH_2 bond elongation in ions having the structure of TS DHA-**2** → **3** is not expected to occur because the resulting ketene–water isomer **1c** lies, see Table 1, far too high in energy. On the other hand, once ions DHA-**3** are formed they are proposed to undergo a facile rearrangement into ions DHA-**4** and these could dissociate by direct bond cleavage into **1a** + CH_2=O. This reaction, however, is not observed for the dissociation of the metastable DHA ions – these exclusively yield **2** + CH_2=O – and we propose that the following kinetic argument provides a rationale.

For simplicity, we assume that a model involving only three isomers suffices. These are DHA-**1**, DHA-**3** and DHA-**6**, where DHA-**3** may dissociate into **1a** + CH_2=O, whereas DHA-**6** may yield **2** + CH_2=O. In this model the barrier between DHA-**3** and DHA-**6** is essential for the product yields: if the corresponding TS (TS DHA-**3** → **4**) would lie near the dissociation limit for **1a** + CH_2=O (and thus also near the rate-determining TS DHA-**2** → **3**), the isomerization DHA-**3** to DHA-**6** and the dissociation DHA-**3** to **1a** + CH_2=O would both fall into the microsecond time frame. In this case the formation of DHA-**6** would compete with the dissociation into **1a** + CH_2=O and both products should be found in the MI spectrum. However, our calculations show that the activation energy for the interconversion DHA-**3** to DHA-**6** is very small indeed. Therefore the isomerization into DHA-**6** will be very fast and the same holds for the dissociation of DHA-**6** into **2** + CH_2=O. In this scenario all reactions are fast except the one corresponding to the first isomerization.

A similar argument applies to the dissociation of DHA-**6a**. This ion can fragment to **2** + CH_2=O at 95 kcal mol^{-1}, but the counterpart constituents $CH_2O^+ + {}^\bullet CH_2COOH$ are also energetically accessible. This dissociation level lies at 112 kcal mol^{-1} when one uses $\Delta_f H$ [$^\bullet CH_2COOH$] = −61.6 kcal mol^{-1} as proposed in the compilation of Ref. [10a]; it becomes even lower, 108 kcal mol^{-1}, if the CBS-QB3 derived value of −57.3 kcal mol^{-1} is used for the radical. Nevertheless, the formation of $CH_2OH^+ + {}^\bullet CH_2COOH$ is not observed at all because dissociation of DHA-**6a** into **2** + CH_2=O will be much faster.

As can be seen from Fig. 2, DHA-**6a** is the global minimum. It has been shown [7] that Mautner's correlation equation for proton bound dimers [18] also applies to hydrogen-bridged radical cations and can be used to estimate their $\Delta_f H$ from known dissociation limits.

For O···H···O hydrogen-bridged radical cation A–H···$B^{\bullet +}$ one obtains [7]:

$$\begin{aligned}\Delta_f H[\text{A–H}\cdots\text{B}^{\bullet +}] = {} & 0.70\{\Delta_f H[\text{AH}^{\bullet +}] + \Delta_f H[\text{B}]\} \\ & + 0.30\{\Delta_f H[\text{HB}^{\bullet +}] + \Delta_f H[\text{A}]\} \\ & - 30.4 \qquad (\text{kcal mol}^{-1}),\end{aligned}$$

where $AH^{\bullet +}$ + B is the cheaper dissociation threshold. Using this equation we obtain $\Delta_f H$ [DHA-**6**] = 69–70 kcal mol^{-1}, which is in agreement with the CBS-QB3 result of 72 kcal mol^{-1}. Note that association of formaldehyde with the *cis–cis* conformer of **2** leads to a stable complex with a double hydrogen bridge, see structure DHA-**6b** in Fig. 3, whose enthalpy lies at 71 kcal mol^{-1}.

Finally we note that ion DHA-**2** could in principle rearrange into DHA-**7**, the precursor ion for the formation of HBRC **4** and CO. The heat of formation of the decarbonylation products **4** + CO actually lies lower in energy than that of **1a** + CH_2=O but the TS connecting DHA-**2** and DHA-**7** lies at 116 kcal mol^{-1}, 3 kcal mol^{-1} higher in energy than TS DHA-**2** → **3**. Thus the fact that the decarbonylation reaction has a significant reverse activation energy may explain why this process is not detected in the MI spectrum of 1,3-dihydroxyacetone.

4. Conclusions

Tandem mass spectrometry based collision experiments reveal that low-energy 1,3-dihydroxyacetone ions (DHA-**1**) dissociate by loss of formaldehyde to produce the ionized enol of acetic acid, i.e., $HOCH_2C(=O)CH_2OH^{\bullet +} \rightarrow CH_2=C(OH)_2^{\bullet +} + CH_2=O$. The mechanism of this seemingly unintelligible reaction has been elucidated with the help of the CBS-QB3 model chemistry. Key intermediate in this dissociation is the ketene–water ion associated via a hydrogen bridge with a formaldehyde molecule, $^\bullet CH_2–C(=O)–O^+(H)–H\cdots O=CH_2$ (DHA-**4/5** in Fig. 2). This ion can undergo an almost barrier-free proton-transport catalysis to produce $CH_2=C(OH)_2^{\bullet +}$ associated with formaldehyde (the global minimum) which then dissociates.

Formation of DHA-**4**, see Fig. 2, is also mechanistically intriguing. After hydrogen bridging of the two hydroxyl groups and concomitant C–C cleavage in DHA-**1**, HBRC DHA-**2** is formed. Next the hydrogen of the H-bridge moves towards the O(H) group and the entire H–O–H···O=CH_2 moiety can shift from the ketene methylene carbon atom to its carbonyl carbon atom to produce DHA-**4**. This rearrangement constitutes the rate-determining step; hence all subsequent reactions will be fast precluding the formation of higher energy products such as the ketene–water ion–dipole complex itself. The calculated energy of the rate-determining transition state, 113.0 kcal mol^{-1}, is in excellent agreement with that (112.5 ± 1.0 kcal mol^{-1}) derived from the experimental appearance energy.

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References

[1] D.K. Böhme, H. Schwarz, Angew. Chem. Int. Ed. 44 (2005) 2.

[2] D.K. Böhme, Int. J. Mass. Spectrom. Ion Process. 115 (1992) 95.

[3] C.Y. Wong, P.J.A. Ruttink, P.C. Burgers, J.K. Terlouw, Chem. Phys. Lett 387 (2004) 204.

[4] J.W. Gauld, L. Radom, J. Am. Chem. Soc. 119 (1997) 9831.

[5] C.Y. Wong, P.J.A. Ruttink, P.C. Burgers, J.K. Terlouw, Chem. Phys. Lett 390 (2004) 176.

[6] (a) For selected recent references see: G. van der Rest, P. Mourgues, H.E. Audier, Int. J. Mass Spectrom. 231 (2004) 83;
(b) X. Wang, J.L. Holmes, Can. J. Chem./Rev. Can. Chim. 83 (11) (2005) 1903–1912;
(c) M.A. Trikoupis, P.J.A. Ruttink, P.C. Burgers, J.K. Terlouw, Eur. J. Mass Spectrom. 10 (2004) 801.

[7] P.C. Burgers, J.K. Terlouw, in: N.M.M. Nibbering (Ed.), Encyclopedia of Mass Spectrometry, vol. 4, Elsevier, Amsterdam, 2005, p. 173.

[8] G. Orlova, V. Blagojevic, D.K. Böhme, J. Phys. Chem. A, in press.

[9] R. Postma, P.J.A. Ruttink, J.K. Terlouw, J.L. Holmes, J. Chem. Soc., Chem Commun. 9 (1986) 683.

[10] (a) Y.-R. Luo, Handbook of Dissociation Energies in Organic Compounds, CRC Press, Boca Raton, 2003;
(b) E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413;
(c) S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.O. Levin, W.G. Maillard, J. Phys. Chem. Ref. Data (Suppl. 1) (1988) 17.

[11] J.L. Holmes, J.K. Terlouw, Org. Mass Spectrom 15 (1980) 383.

[12] (a) J.W. Ochterski, G.A. Petersson, J.A. Montgomery Jr., J. Chem. Phys. 104 (1996) 2598;
(b) J.A. Montgomery Jr., M.J. Frisch, J.W. Ochterski, G.A. Petersson, J. Chem. Phys. 112 (2000) 6532.

[13] R. Lee, P.J.A. Ruttink, P.C. Burgers, J.K. Terlouw, Can. J. Chem. 83 (2005) 1847.

[14] H.F. van Garderen, P.J.A. Ruttink, P.C. Burgers, G.A. McGibbon, J.K. Terlouw, Int. J. Mass Spectrom. Ion Process. 121 (1992) 159.

[15] L.M. Fell, J.T. Francis, J.L. Holmes, J.K. Terlouw, Int. J. Mass Spectrom. Ion. Process. 165/166 (1997) 179.

[16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C. 02, Gaussian, Inc., Wallingford CT, 2004.

[17] M.F. Guest, J.H. van Lenthe, J. Kendrick, K. Schoffel, P. Sherwood, with contributions from R.D. Amos, R.J. Buenker, H.J.J. van Dam, M. Dupuis, N.C. Handy, I.H. Hillier, P.J. Knowles, V. Bonacic-Koutecky, W. von Niessen, R.J. Harrison, A.P. Rendell, V.R. Saunders, A.J. Stone, D.J. Tozer, A.H. de Vries, GAMESS-UK is a package of ab initio programs. The package is derived from the original GAMES S code due to M. Dupuis, D. Spangler, J. Wendolowski, NRCC Software Catalogue 1, vol. 1, Program No. QG01 (GAMESS), 1980.

[18] M. Meot-Ner (Mautner), J. Am. Chem. Soc. 106 (1984) 1257, and references cited therein.