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Exploring the potential energy surface of ion–molecule pairs by experiment and by theory: acetaldehyde and methanol

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Abstract

The energy barrier for the keto–enol isomerization of the isolated acetaldehyde ion to vinyl alcohol lies above its lowest dissociation limit and so the spontaneous isomerization is never observed. However, it has been shown that the distonic methanol ion can ionize the acetaldehyde molecule and greatly lower the energy barrier of the keto–enol isomerization. The present study involved two systems in which the acetaldehyde was associated with the distonic methanol cation, $^{\bullet}CH_2OH_2{}^{+}$, and with its conventional isomer, $CH_3OH^{+\bullet}$, in stable and metastable adducts. The isomerization barrier for acetaldehyde was lowered by association with $^{\bullet}CH_2OH_2{}^{+}$; in contrast, the $CH_3OH^{+\bullet}$ ion did not facilitate the rearrangement of acetaldehyde to its enol ion. Tandem mass spectrometry combined with ab initio calculations was applied to investigate the two systems. Potential energy surface diagrams were obtained by MP2/6-31+g(d) and B3-LYP/6-31+g(d) calculations to further elucidate the reaction mechanisms.

Keywords: Ion–molecule complexes; Mechanisms; Rearrangement; Structure

1. Introduction

For many years, it has been known that the keto–enol isomerization of an ionized aldehyde or ketone in the gas phase involves a large energy barrier [1–5]. These barriers generally lie at energy above the lowest dissociation threshold for the carbonyl compound and so the isomerization is never directly observed for the isolated ion. However, when such ions are electrostatically bound to a substrate molecule, these barriers can be reduced to below the first dissociation threshold. It is now becoming apparent that odd-electron ion–molecule pairs perform unexpected reactions in which the ion undergoes rearrangements catalyzed either homogeneously or heterogeneously by its neutral partner or substrate. Much of this work has involved the identification of the mechanisms for the ion isomerizations.

1.1. Proton transport catalysis (PTC)

This catalytic mechanism was first reported by Böhme [6]. As an example, the $CH_4O^{+\bullet}$ ion has two isomers, the conventional methanol ion and the thermochemically more stable (by 32 kJ/mol) distonic isomer, the methylene oxonium ion, $^{\bullet}CH_2OH_2{}^{+}$. In isolated $CH_3OH^{+\bullet}$ ions, the barrier for rearrangement to the distonic form lies above the ion's first dissociation limit, to $^{+}CH_2OH + H^{\bullet}$, and so the distonic isomer is inaccessible at any energy [7–10]. However, if the methanol ion is electrostatically bound to a water molecule (I), it can transfer a proton to the latter, to give (II):

$$\underset{\text{(I)}}{CH_3OH^{+\bullet}}/H_2O \rightarrow \underset{\text{(II)}}{^{\bullet}CH_2OH/^{+}H_3O} \rightarrow \underset{\text{(III)}}{^{\bullet}CH_2OH_2{}^{+}}/H_2O$$

In (II), the proton can formally return to the carbon or oxygen atom in the $^{\bullet}CH_2OH$ radical but proton transfer to O gives the thermochemically more stable distonic methanol ion–water pair, $^{\bullet}CH_2OH_2{}^{+}/H_2O$. The catalyzed reaction is calculated to proceed with less than half the

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activation energy of the unimolecular rearrangement of $CH_3OH^{+\bullet}$.

Such catalytic processes involving H^+ transport between partners have to meet a necessary criterion which has been established by the calculations of Chalk and Radom [11] namely that when the proton can return to two sites in the radical, the proton affinity (PA) of the catalyst (H_2O in the above example) must lie between the PA values for the radical and heteroatom sites. This condition is obeyed in the above case, i.e., PA[H_2O] = 682 kJ/mol [12]; PA[$^\bullet CH_2OH$] at O = 695 kJ/mol [12] and at C = 663 kJ/mol [12].

1.2. $H^\bullet$-atom transfer mechanism (ATM)

This mechanism is also called the “Quid pro Quo” (QpQ) mechanism [13]. In this process, the ion accepts a H atom from the neutral substrate, forming a protonated species which then donates a different H atom back to the neutral radical. This ATM model has been described in the $CH_3CHO^{+\bullet}/CH_3OH$ system by van der Rest et al. [14] with calculations at the UMP2/6-31G** level of theory, and is shown below:

$$CH_3CHO^{+\bullet}\cdots O(\underline{H})CH_3 \rightarrow CH_3CHO\underline{H}^{+}\cdots {}^\bullet OCH_3$$
$$\rightarrow CH_2CHO\underline{H}^{+\bullet}\cdots O(H)CH_3$$

In the above scheme, the acetaldehyde radical cation isomerizes into the vinyl alcohol ion as well as exchanging a $H^\bullet$ atom with the methanol molecule. The underlined $H^\bullet$ atom shifts from methanol to the aldehydic O atom and then a methyl $H^\bullet$ atom of acetaldehyde transfers back to the methoxy radical.

1.3. Spectator mechanism

This mechanism differs from PTC and ATM in that there is no atom exchange between the ion and the catalyst, i.e., the configuration of the catalyst substrate does not change throughout. For example, computations by Radom and coworkers [8] have described the water-catalyzed interconversion of the methanol ion to its distonic isomer undergoing the spectator mechanism. The TS for the 1,2-H shift is lower in energy than the barrier for the isomerization of the isolated methanol ion; the water molecule is elelctrostatically bound to the shifted $H^\bullet$ atom and the water “drags” the methyl $H^\bullet$ of methanol across the C–O bond. This mechanism was first illustrated by experiment by Tu and Holmes [15].

In a previous study [13,14], the enol or keto cations of acetaldehyde were formed in an FT-ICR cell and allowed to react with a neutral methanol molecule. Under these conditions, the methanol molecule was found to catalyze the isomerization of the acetaldehyde ion to its isomeric form. The generation of keto ions can be achieved by direct electron impact ionization of the molecule, while enol ions were made in an ion source by the fragmentation of an appropriate ionized cyclic alcohol (e.g., by loss of an olefin) [16] or by a McLafferty rearrangement of a selected carbonyl compound [16,17].

In the present study, we have investigated the keto–enol isomerization of acetaldehyde when associated with ionized methanol and its distonic isomer in a stable or metastable ion–molecule pair. The method for making such stable ion–molecule pairs is as follows. Proton-bound dimers are easily obtained from a high pressure ion source and they can be made to lose a radical under collision-induced dissociation (CID) conditions [15,18]. These CID fragmentations can produce the ion–molecule complexes of interest, namely solvated conventional or distonic odd electron ions. The advantage of this method is that the majority of the ions are stable but with some having sufficient internal energy to undergo competing metastable dissociations. Appropriate isotopic labeling and collision-induced dissociation mass spectra of the above stable ions allows one to explore the rearrangement processes that they can undergo.

This paper presents an experimental study of the aldehyde/$CH_4O^{+\bullet}$ ion–molecule complexes, formally represented as $CH_3CHO/{}^+H_2OCH_2{}^\bullet$ ion **1** and $CH_3CHO/{}^{+\bullet}HOCH_3$ ion **2**. They were generated in the mass spectrometer by selecting the appropriate fragment ions in the CID mass spectra of proton-bound molecular pairs. To aid the explanation of the experimental results, potential energy surfaces (PES) for the species were obtained by theoretical calculations. The PES thus constructed should be compatible with the experimental observations in terms of the observed competing metastable ion fragmentations, the relative abundances of the product ions and the collision sensitivity of the metastable ion peaks and the detailed appearance of the CID mass spectra. Furthermore, they should be compatible with the fate of isotopic labels among the dissociation products. The PES also identifies the possible presence of high isomerization barriers that effectively eliminate some plausible rearrangement pathways.

2. Experimental and theoretical section

All experiments were carried out on a modified ZAB-3F tandem mass spectrometer [19] with BEE geometry (VG Analytical, Manchester, U.K.). Metastable ion (MI) and collision-induced dissociation (CID) mass spectra of the proton-bound dimer and the ion–molecule pairs were acquired in the second field-free region (2FFR) and third field-free region (3FFR) of the mass spectrometer, respectively. The ion accelerating voltage was 8 kV. In the 2FFR and 3FFR helium was used as the collision gas for the CID experiments. All spectra were recorded with the ZABCAT program developed by Mommers Technologies [19].

The proton-bound dimer of acetaldehyde and propanol was generated by admitting the mixed regents $CH_3CH_2CH_2OH$ and CH_3CHO into a high pressure ion source at a total observed pressure of ca. 8×10^{-5} mbar, indicating an ion pressure of 0.5 mbar [20]. The proton-bound dimer $CH_3CHO{\cdots}H^+{\cdots}O(H)CH_2CH_2CH_3$ ($m/z = 105$) was mass-selected by the magnet and collisionally activated in the second field-free region. The fragment ion $[CH_3CHO/^{\bullet}CH_2OH_2{}^+]$ (m/z 76) was produced by loss of $CH_3CH_2{}^{\bullet}$ from the precursor ion (m/z 105) and it was transmitted into the third field-free region to study its MI and CID characteristics.

A similar experiment was used for the acetaldehyde/dimethyl ether proton-bound dimer, $CH_3CHO{\cdots}H^+{\cdots}O(CH_3)_2$ (m/z 91), in order to collisionally generate labeled $[CH_3CHO/CH_3OH^{+\bullet}]$ (m/z 76) by specific loss of $CH_3{}^{\bullet}$ from the ether. An experiment using $CD_3CHO{\cdots}H^+{\cdots}O(CH_3)_2$ (m/z 94) showed that it was an ether methyl group that was lost in the CID. Dimethyl ether was introduced through the gas inlet at an observed pressure of 5×10^{-5} mbar producing 0.3 mbar in the high pressure ion source.

CH_3CHO, $CH_3CH_2CH_2OH$, $(CH_3)_2O$, and the isotopically labeled compounds, CD_3CHO, CD_3CDO, $CH_3CH_2CD_2OH$, $CH_3CH_2{}^{13}CH_2OH$ were used to generate various isotopomeric ion–molecule pairs. The unlabeled chemicals were purchased from Aldrich and all the labeled samples, 99.5–99.9% isotope purity, were obtained from CDN Isotopes (Montreal, QC, Canada) and were used without further purification.

GAUSSIAN 98 programs were used to perform standard ab initio molecular orbital calculations to investigate the potential energy surface. Optimized geometries and the energies of all minima and transition states were calculated at the MP2/6-31+G(D) level of theory. Zero point energies obtained from vibrational frequencies at the same level of theory were scaled by a factor of 0.943 [21]. A potential energy profile was also obtained from density functional theory B3-LYP/6-31+G(D) to compare with the PES acquired by the MP2/6-31+G(D) calculations. The differences between the two levels of theory are discussed later. Finally, a single point energy calculation at the G3 level of theory was applied to obtain accurate relative energies of the optimized ion structures at MP2/6-31+G(D) and B3-LYP/6-31+G(D), respectively.

3. Results and discussion

3.1. Experimental observations for ion **1** $[CH_3CHO/^{\bullet}CH_2OH_2{}^+]$ and ion **2** $[CH_3CHO/CH_3OH^{+\bullet}]$

3.1.1. $[CH_3CHO/^{\bullet}CH_2OH_2{}^+]$ ion **1**

An ion of formal structure **1** was obtained by the collision-induced loss of a $CH_3CH_2{}^{\bullet}$ radical from the proton-bound dimer $CH_3CHO{\cdots}H^+{\cdots}O(H)CH_2CH_2CH_3$ (m/z 105). The PA of propanol, 786.5 kJ/mol, is higher than that of acetaldehyde, 768.5 kJ/mol, and so the proton is preferentially attached to the alcohol to give protonated propanol electrostatically bound to an acetaldehyde molecule, i.e., $CH_3CHO/{}^+H_2OCH_2CH_2CH_3$. In the CID mass spectrum of this proton-bound dimer, m/z 105, the major peaks are protonated propanol (m/z 61, 100%), protonated acetaldehyde (m/z 45, 23%), and the peak for $CH_3CH_2{}^{\bullet}$ loss (m/z 76). The first two reactions are the only MI processes, showing that rearrangement of the proton bound dimer does not take place at internal energies up to those for MI dissociations; m/z 76 appears only when collision gas is admitted.

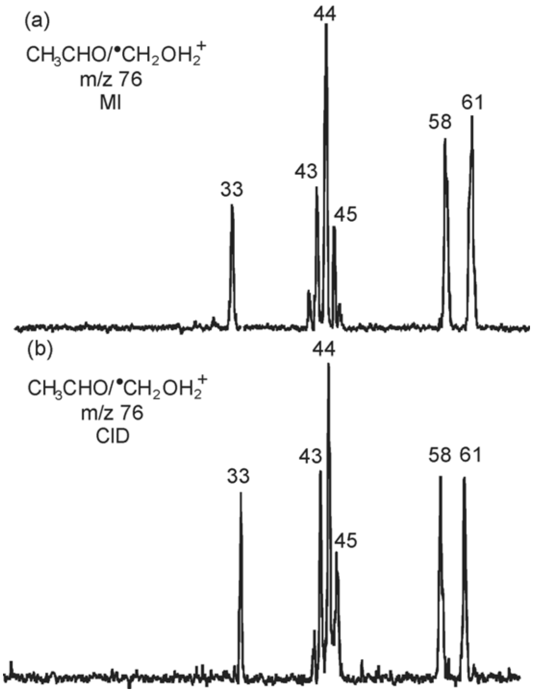


Fig. 1. MI and CID mass spectra of $CH_3CHO/^{\bullet}CH_2OH_2{}^+$.

$$CH_3CHO \cdots \underset{m/z\,105}{H^+O(H)CH_2CH_2CH_3}$$

$$\to \underset{m/z\,76}{[CH_3CHO/^{\bullet}CH_2O(H)H^+]} + CH_3CH_2{}^{\bullet}\,(\mathrm{CID}) \qquad (1)$$

The MI spectrum of ion **1** (Fig. 1a) indicates that there are six competing dissociation reactions of m/z 76: the losses of $CH_3{}^{\bullet}$ (m/z 61), H_2O (m/z 58), and the formation of CH_3CHOH^+ (m/z 45), CH_3CO^+ (m/z 43), $CH_3OH_2{}^+$ (m/z 33); the base peak, m/z 44, has been determined to be the vinyl alcohol ion (see below).

In the CID mass spectrum of ion **1** (Fig. 1b) the intensity of the peak at m/z 45, CH_3CHOH^+, is increased, i.e., the formation of CH_3CHOH^+ is collision sensitive, being a simple bond cleavage in ion **1**. The PA of CH_3CHO at O is 768.5 kJ/mol, which is much higher than the PA of $^{\bullet}CH_2OH$, 695 kJ/mol, so that the structure of the stable ion **1** is better represented as $CH_3CHOH^+{\cdots}O(H)CH_2{}^{\bullet}$. However, the peak corresponding to the formation of the m/z 44 ion is not collision sensitive, indicating that ion **1** rearranges before it fragments.

The dissociation channel leading to the enol form of ionized acetaldehyde, the vinyl alcohol ion, is energetically the most favourable process. If the ion m/z 44 has the enol

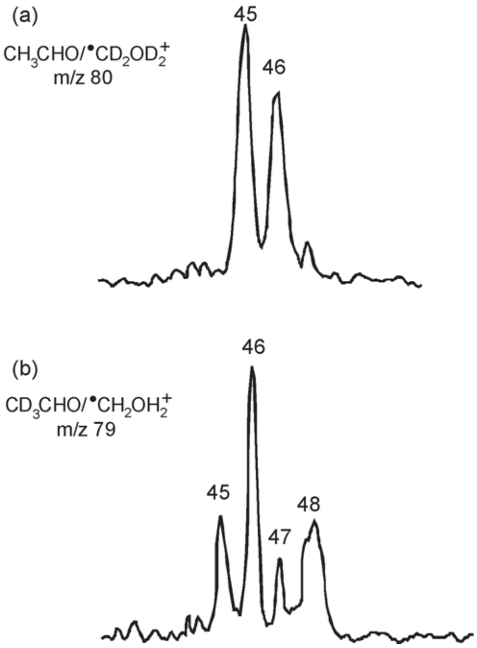


Fig. 2. (a) The major fragment ion of $CH_3CHO/^{\bullet}CD_2OD_2^+$ gives *m*/*z* 45, CH_2CHOD^+. (b) The major fragment ion of $CD_3CHO/^{\bullet}CH_2OH_2^+$ gives *m*/*z* 46, CD_2CHOH^+.

structure, the dissociation threshold energy is at 569 kJ/mol (from $\Delta_f H[CH_2CHOH^{+\bullet}] = 771$ kJ/mol, $\Delta_f H[CH_3OH] = -202$ kJ/mol) [22]. This is lower than the dissociation limit, 576 kJ/mol, for the formation of the protonated acetaldehyde ion *m*/*z* 45 (from $\Delta_f H[CH_3CHOH^+] = 595$ kJ/mol, $\Delta_f H[^{\bullet}CH_2OH] = -19$ kJ/mol) [22]. If the *m*/*z* 44 ion had the keto structure, the threshold energy for this dissociation would be much higher, at 619 kJ/mol (from $\Delta_f H[CH_3CHO^{+\bullet}] = 821$ kJ/mol, $\Delta_f H[CH_3OH] = -202$ kJ/mol) [22]. Thus in the MI mass spectrum of ion **1**, the base peak would be peak *m*/*z* 45 if the $CH_3CHO^{+\bullet}$ ion had not isomerized. That the enol ion is produced is also supported by the results of isotopic labeling.

The isotopically labeled ion–molecule pairs, $[CD_3CHO/^{\bullet}CH_2OH_2^+]$, **1**-d$_3$ (*m*/*z* 79), $[CD_3CHO/^{\bullet}CD_2OH_2^+]$, **1**-d$_5$ (*m*/*z* 81), $[CH_3CHO/^{\bullet}CD_2OH_2^+]$, **1**-d$_2$ (*m*/*z* 78), $[CH_3CHO/^{\bullet}CD_2OHD^+]$, **1**-d$_3$ (*m*/*z* 79), $[CH_3CHO/^{\bullet}CD_2OD_2^+]$, **1**-d$_4$ (*m*/*z* 80) were examined to assign the structure of the above *m*/*z* 44 ion as that of vinyl alcohol. The MI mass spectrum of $[CH_3CHO/^{\bullet}CD_2OD_2^+]$, **1**-d$_4$ (*m*/*z* 80) (Fig. 2a) shows the most intense peak at *m*/*z* 45, to which the structure $CH_2CHOD^{+\bullet}$ is assigned; if the keto ion were the major product, it would have resulted in *m*/*z* 44, $CH_3CHO^{+\bullet}$, being observed instead. Similar observations were found for the other labeled pairs. For example, Fig. 2(b) shows the MI mass spectrum of $[CD_3CHO/^{\bullet}CH_2OH_2^+]$, **1**-d$_3$ (*m*/*z* 79), with the base peak at *m*/*z* 46, i.e., $CD_2CHOH^{+\bullet}$, not $CD_3CHO^{+\bullet}$ (*m*/*z* 47). The experimental data for all labeled ion–molecule pairs are shown in Table 1. The results are explained as follows. Before the ion–molecule pair **1**, $[CH_3CHO\cdots H^+\cdots OHCH_2^{\bullet}]$, dissociates to the vinyl alcohol ion and methanol, a $H^{\bullet}$ atom from CH_3CHO moves to the $^{\bullet}CH_2OH$ radical via a 1,6-H shift. This process involves TS3 on the PES (see Fig. 7) and the discussion of the computations. Furthermore, two $H^{\bullet}$ atoms of CH_3CHOH^+ in ion **1**-d$_2$, exchange with D atoms at the radical site of $^{\bullet}CD_2OH$ during such a rearrangement.

One question remains: could *m*/*z* 44 possibly be the carbene ion $CH_3COH^{+\bullet}$, even though it is unlikely to be produced on energetic grounds ($\Delta_f H[CH_3COH^{+\bullet}] = 865$ kJ/mol [22])? To test this, the ion $CH_3COH^{+\bullet}/CH_3OH$, ion **3**, was made by CID loss of an ethyl radical from the proton-bound dimer, $CH_3CH_2C(CH_3){=}O\cdots H^+\cdots O(H)CH_3$. Its MI mass spectrum (Fig. 3) shows four major products: protonated methanol (*m*/*z* 33), the acetyl ion (*m*/*z* 43), water loss (*m*/*z* 58) and methyl loss (*m*/*z* 61). However, it does not produce any *m*/*z* 44, $CH_3COH^{+\bullet}$, whose generation cannot compete energetically with the other dissociation channels. Therefore, the carbene ion can be ruled out.

An experiment using the ^{13}C labeled ion $CD_3CHO/^{13\bullet}CH_2O(D)H^+$, *m*/*z* 81 (Fig. 4) proved that the lost methyl is from the methanol portion of the ion. The kinetic energy release (obtained from the width of the peak at half-height, $T_{0.5}$) associated with the $CH_3^{\bullet}$ radical loss has been measured as 67 meV, indicative of a reverse energy barrier. The structure assigned to the fragment ion for $CH_3^{\bullet}$ loss from ion **1** is $CH_3C^+(OH)_2$, protonated acetic acid, $\Delta_f H = 313$ kJ/mol. This low energy species is indeed the likely product, as will be discussed later. The production of $CH_3OH_2^+$ and isotopomers involves formal H/D exchange between the acetaldehyde and methanol species.

3.1.2. [$CH_3CHO/CH_3OH^{+\bullet}$] ion 2

The CID mass spectrum of the proton bound acetaldehyde–dimethyl ether dimer $CH_3CHO\cdots H^+\cdots O(CH3)_2$ (*m*/*z* 91) ion showed two major peaks, namely protonated dimethyl ether (*m*/*z* 47), protonated acetaldehyde (*m*/*z* 45), and the minor $CH_3^{\bullet}$ loss peak (*m*/*z* 76), the reaction is shown below:

$$\underset{m/z\,91}{CH_3CHO\cdots H^+O(CH_3)_2}$$

$$\rightarrow \underset{m/z\,76}{[CH_3CHO/CH_3OH^{+\bullet}]} + CH_3^{\bullet}\ (\text{CID}) \qquad (2)$$

The methyl radical lost could come from either molecule and so deuterium labeling was used to identify the methyl group, e.g., $CD_3CHO\cdots H^+\cdots O(CH_3)_2$, **2**-d$_3$, $CD_3CDO\cdots H^+\cdots O(CH_3)_2$, **2**-d$_4$, and $CD_3CDO\cdots D^+\cdots O(CH_3)_2$, **2**-d$_5$, only lost $^{\bullet}CH_3$ in their CID mass spectra, showing that only an ether methyl group is involved.

Compared with its isomer **1**, the MI mass spectrum of ion **2** (and its isotopomers) is simpler. There are four competing dissociation channels, giving protonated acetaldehyde (*m*/*z* 45), the acetaldehyde ion (*m*/*z* 44), protonated methanol (*m*/*z* 33), and $CH_3^{\bullet}$ loss (*m*/*z* 61). In contrast with the mass spectra of its isomer, ion **1**, the MI and CID mass spectra of ion **2** show

Table 1
Fragmentations of labeled acetaldehyde/distonic methanol ion–molecule pairs in the MI spectra

Precursor ion *m*/*z*	Ion–molecule pair *m*/*z*	Fragments of ion–molecule pair *m*/*z*				
		Protonated methanol	Vinyl alcohol	Protonated acetaldehyde	$-H_2O$	–methyl
$(CH_3CHO)H^+$, $(HOCH_2CH_2CH_3)$, 105	$[CH_3CHO/{}^{\bullet}CH_2OH_2{}^+]$, 76	33	44	45	58	61
$(CH_3CHO)H^+$, $(HOCD_2CH_2CH_3)$, 107	$[CH_3CHO/{}^{\bullet}CD_2OH_2{}^+]$, 78	33 34 35	44	45 46	59 60	61 62 63
$(CD_3CHO)H^+$, $(HOCH_2CH_2CH_3)$, 108	$[CD_3CHO/{}^{\bullet}CH_2OH_2{}^+]$, 79	33 34	45 46 47	48	60 61	62 63 64
$(CH_3CHO)D^+$, $(DOCD_2CH_2CH_3)$, 109	$[CH_3CHO/{}^{\bullet}CD_2OD_2{}^+]$, 80	35 36 37	44 45	46 47	60 61 62	63 64 65
$(CD_3CHO)H^+$, $(HOCD_2CH_2CH_3)$, 110	$[CD_3CHO/{}^{\bullet}CD_2OH_2{}^+]$, 81	35 36 37	45 46 47	48	61 62 63[a]	63[a] 64 65
$(CH_3CHO)H^+$, $(HO^{13}CH_2CH_2CH_3)$, 106	$[CH_3CHO/{}^{13\bullet}CH_2OH_2{}^+]$, 77	34	44	45	59	61 (major) 62 (minor)
$(CH_3CHO)D^+$, $(DO^{13}CH_2CH_2CH_3)$, 108	$[CH_3CHO/{}^{13\bullet}CH_2OD_2{}^+]$, 79	35 36	45	46	59 60	62 63 64
$(CD_3CHO)H^+$, $(HO^{13}CH_2CH_2CH_3)$, 109	$[CD_3CHO/{}^{13\bullet}CH_2OH_2{}^+]$, 80	34 35 36	45 46	48	62[b]	62[b] 63 64
$(CD_3CHO)H^+$, $(DO^{13}CH_2CH_2CH_3)$, 110	$[CD_3CHO/$, ${}^{13\bullet}CH_2ODH^+]$, 80	35 36 37	45 46 47	48	62	63 64 65
$(CD_3CHO)D^+$, $(DO^{13}CH_2CH_2CH_3)$, 111	$[CD_3CHO/{}^{13\bullet}CH_2OD_2{}^+]$, 82	36 37 38	47	49	63	64 65 66

[a] *m*/*z* 63 ions are a mixture of the losses of H_2O and ${}^{\bullet}CD_3$ in the MI mass spectrum of $[CD_3CHO/{}^{\bullet}CD_2OH_2{}^+]$ (*m*/*z* 81).

[b] *m*/*z* 62 ion results from the losses of H_2O and ${}^{\bullet 13}CD_2H$ in the MI mass spectrum of $[CD_3CHO/{}^{13\bullet}CH_2OH_2{}^+]$ (*m*/*z* 80).

that hydrogen and deuterium atoms do not mix (see Fig. 5, the MI mass spectrum of $CD_3CHO/CH_3OH^{+\bullet}$, **2**-d$_3$ *m*/*z* 79). The base peak is protonated acetaldehyde, CD_3CHOH^+ (*m*/*z* 48), and the smaller peak *m*/*z* 47 has to be the acetaldehyde radical cation, not the vinyl alcohol ion, even though it is more energetically favoured than protonated acetaldehyde, see the discussion of ion **1** above. The H/D atoms in *m*/*z* 47, $CD_3CHO^{+\bullet}$, have retained their original positions, indicating no rearrangement of ion **1** to the enol form. There is an exclusive peak at *m*/*z* 33, $CH_3OH_2{}^+$, and only one methyl loss peak, M-18, corresponding to the $CD_3{}^{\bullet}$ group. The CID mass spectrum of the **2**-d$_3$ ion showed that the M-18 peak is collision sensitive and very likely arises from a simple C–C bond cleavage. The M-18 peak cannot arise from loss of H_2O because the MI

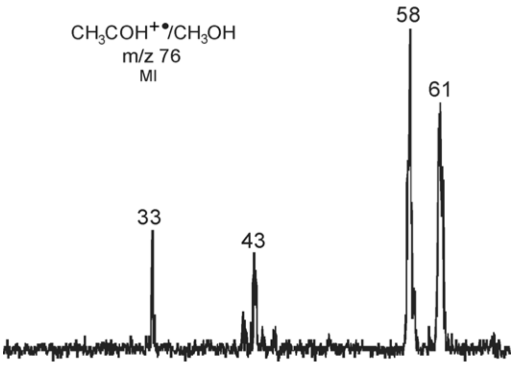


Fig. 3. MI mass spectrum of the $CH_3COH^{+\bullet}/OHCH_3$ ion.

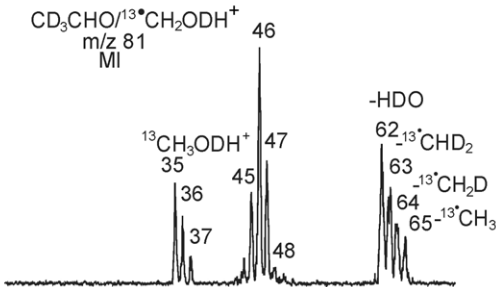


Fig. 4. MI mass spectrum of labeled $CD_3CHO/{}^{13\bullet}CH_2ODH^+$.

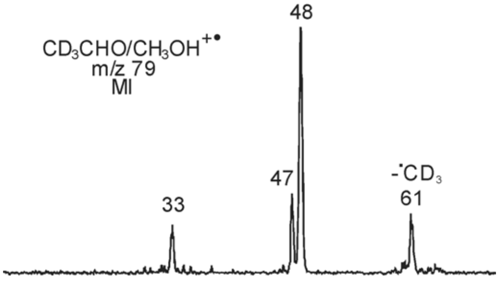


Fig. 5. MI mass spectrum of the ion $CD_3CHO/CH_3OH^{+\bullet}$.

mass spectrum of the ion $CD_3CDO/CH_3OD^{+\bullet}$ (*m/z* 81), **2**-d_5, gave an intense peak M-18 (*m/z* 63), but no M-20 ($-D_2O$) peak or M-19 ($-$HDO).

3.2. Theoretical calculations

The two ions, $[CH_3CHO/{}^\bullet CH_2OH_2{}^+]$ and $[CH_3CHO/CH_3OH^{+\bullet}]$, display different chemistries in their mass spectra. Thus these two systems do not communicate with each other, presumably because there is a high energy barrier to their interconversion. Theoretical calculations were performed to investigate this and to produce a PES for each ion and its fragmentations.

3.2.1. The $[CH_3CHO/{}^\bullet CH_2OH_2{}^+]$ system

The energy profile is shown schematically in Fig. 7. The optimized structure of ion **1** is $CH_3CHO\cdots H^+\cdots O(H)CH_2{}^\bullet$, Stable State IV, in which the proton is close to the aldehydic oxygen, rather than to the methanol oxygen; the former bond length $(CH_3CH)O–H$ is 1.057 Å, the latter O–H length is 1.487 Å (see Fig. 6 a). This is in keeping with the PA of CH_3CHO being greater than that for ${}^\bullet CH_2OH$ at oxygen (see also Section 3.1 above). Ion IV rearranges to the vinyl alcohol–methanol ion, $CH_2CHOH^{+\bullet}\cdots O(H)CH_3$, complex V, via a cyclic transition state (TS) 3. This requires only about 115 kJ/mol and lies below the dissociation threshold of IV to form protonated acetaldehyde and the hydroxyl methyl radical, 136 kJ/mol. The relative energies given above are obtained at the MP2/6-31+g(d) level of theory (see Fig. 7). The energy for the isolated acetaldehyde ion to vinyl alcohol isomerization is at 215 kJ/mol [2] and lies above the dissociation limit of the keto ions (103 kJ/mol) [2]. Note that TS3, the seven-membered ring structure, would be favoured by entropy considerations. Complex V then dissociates to produce the vinyl alcohol ion and a methanol molecule, the dissociation limit for which is ∼130 kJ/mol; this process involves the low energy barrier TS3 and is the competing dissociation channel of lowest energy, giving rise to the most intense peak in the MI mass spectrum of ion **1**. Thus the initial aldehyde has been isomerized to its enol-form by transferring a proton and a $H^\bullet$ atom. We believe that the free radical site functions as a good $H^\bullet$ or H^+ accepter and facilitates the enolization of acetaldehyde.

The formation of the protonated methanol ion can be via two pathways. In the first, ion V rearranges to complex VI, $CH_3CO^\bullet\cdots H^+OHCH_3$, via a 1,2-H shift in the vinyl alcohol to generate the acetyl radical and protonated methanol. This process requires a large energy barrier TS5 (∼193 kJ/mol) for the internal 1,2-H shift. There is another more facile pathway, namely the isomerization of complex IV to VI via a 1,5-H shift, transition state TS4, at 145 kJ/mol and so is more accessible than TS5. This explains why the protonated methanol in the MI mass spectrum of $CD_3CHO/{}^{13\bullet}CH_2OHD$ (Fig. 4) is chiefly ${}^{13}CH_3D^+OH$ but with some evidence of H, D exchanges.

We also observed an intense water loss peak in the above experiments, in the complex IV, a species that when initially made in the mass spectrometer does not contain a H_2O species. An S_N2 mechanism has been considered for this water loss process. After complex IV converts to V, the rotation of CH_3OH along the O–C bond, TS6a, allows the protonated methanol to turn around, ready to be back-attacked by $CH_2CHOH^{+\bullet}$, the intermediate complex (INT, in Fig. 7) contains three species, and TS6b leads to dissociation to H_2O and $CH_2CHOCH_3{}^{+\bullet}$.

The experimental results indicate that the production of the $(M\text{-}15)^+$ ion is due to the methanol methyl radical loss, and the mechanism explored by the calculations is as follows. Interconversion between complex VI and the carbene ion with methanol $CH_3C^{+\bullet}(OH)\cdots OHCH_3$, complex VII, takes place via transition state TS7 (∼107 kJ/mol). In TS8, the extension of the C–O bond in methanol leads to the OH moving towards the carbonyl C of $CH_3COH^{+\bullet}$. VII then converts to complex IX, protonated acetic acid electrostatically bound to the methyl radical, which is a very stable species lying at about −25 kJ/mol on PES **1** (even 25 kJ lower than the Stable State V). Structure IX fragments readily to the products, protonated acetic acid and methanol (∼28 kJ/mol).

Kinetic energy release (KER) measurement experiments [23] were made on all the MI ion peaks and KER values ($T_{0.5}$) are consistent with the TS heights on the PES **1** (Fig. 7). The $CH_3{}^\bullet$ loss ion had the largest KER, 67 meV, in keeping with it having the largest reverse energy barrier on the PES **1**, the energy difference between TS4 (the highest transition state in its pathway) and the dissociation limit, 117 kJ/mol. This is compatible with the smaller KER for the H_2O loss ion, 48 meV, corresponding to a reverse energy barrier of 52 kJ/mol, the difference between the products' energy and that of TS6b. However, it was surprising to find that the generation of the protonated methanol ion (*m/z* 33) had the lowest KER, 8 meV, although it is not a simple bond cleavage process. This may be due to the tight cyclic transition state TS4. In order to form the complex VI from TS4, a heavy methyl group must rotate to reform the proton bound pair, and thus a large rotational energy component is involved, resulting in a smaller translational energy release in the products. Alternatively, at the energy corresponding to TS4, there may be little coupling between the degrees of freedom in

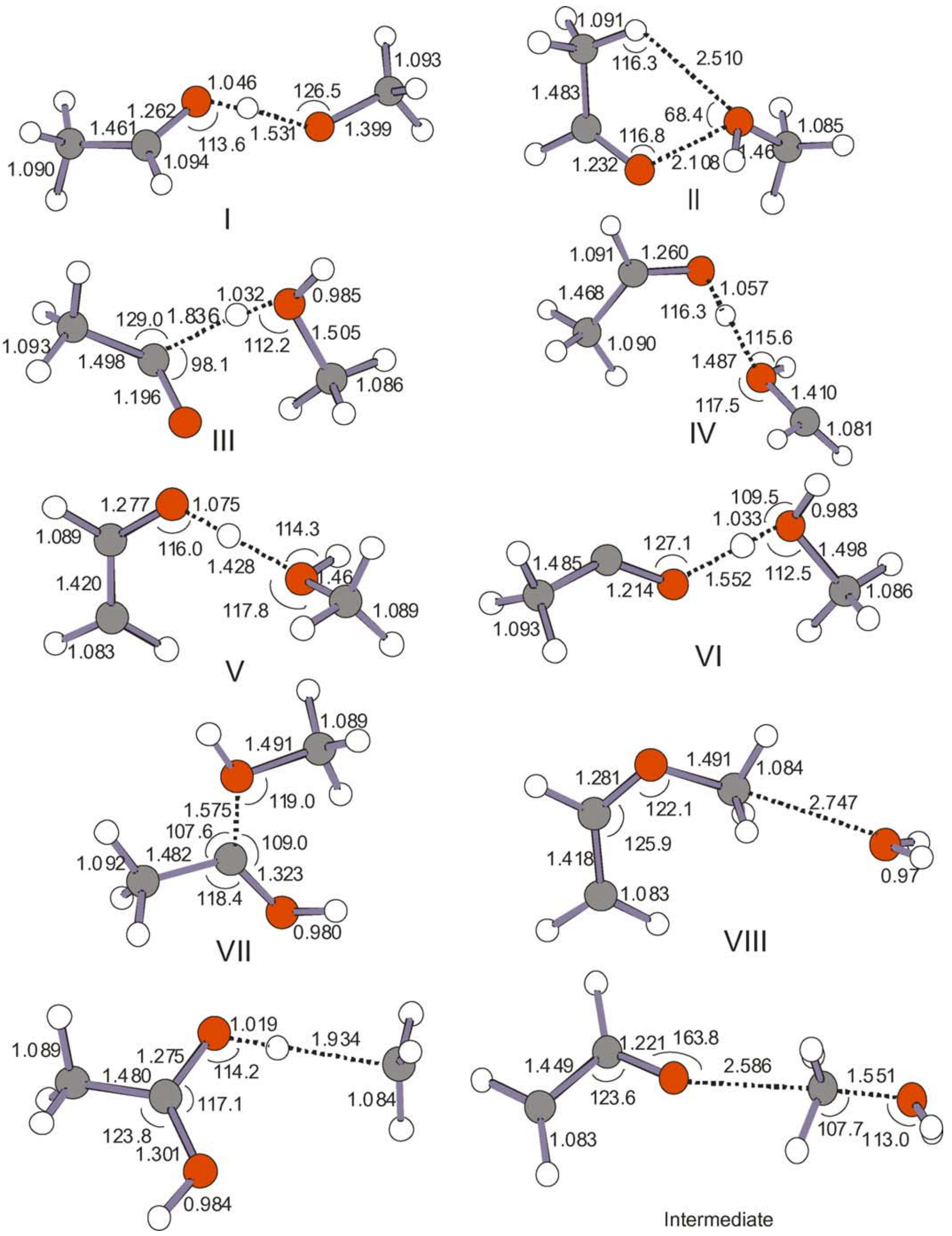


Fig. 6. (a) Optimized geometries of the Stable States at MP2/6-31+G(D).

the ion and neutral moieties, i.e., the radical may be free to move around the $CH_3OH_2{}^+$ ion, leading to a relatively small KER.

3.2.2. The [$CH_3CHO/CH_3OH^{+\bullet}$] system

The major dissociation thresholds on the PES of ion **2** (Fig. 8) are the formation of CH_3CHOH^+ and a methoxyl radical (~171 kJ/mol), $CH_3CHO^{+\bullet}$ and methanol (~180 kJ/mol). The stable complex I, $CH_3CHOH^+\cdots{}^\bullet OCH_3$, is able to rearrange to complex II, $CH_3CHO^{+\bullet}\cdots HOCH_3$. However, no transition state structure has been found to connect these two minima; other workers have encountered the same problem [13,14]. In the complex II, the O atom of CH_3OH is associated with the carbonyl O and methyl H of $CH_3CHO^{+\bullet}$ in the form of a five-membered ring structure. The computational difficulty arises when I converts to II, the charge centre migrates from the proton to the aldehydic C atom and at the same time a $H^\bullet$ radical moves to $CH_3O^\bullet$. Because protonated methanol is observed in the MI mass spectrum, this transition state, TS1/2, should be below the dissociation limits of the precursor ion–molecule complex I. Haranczyk et al. [13] found a minimum energy crossing point

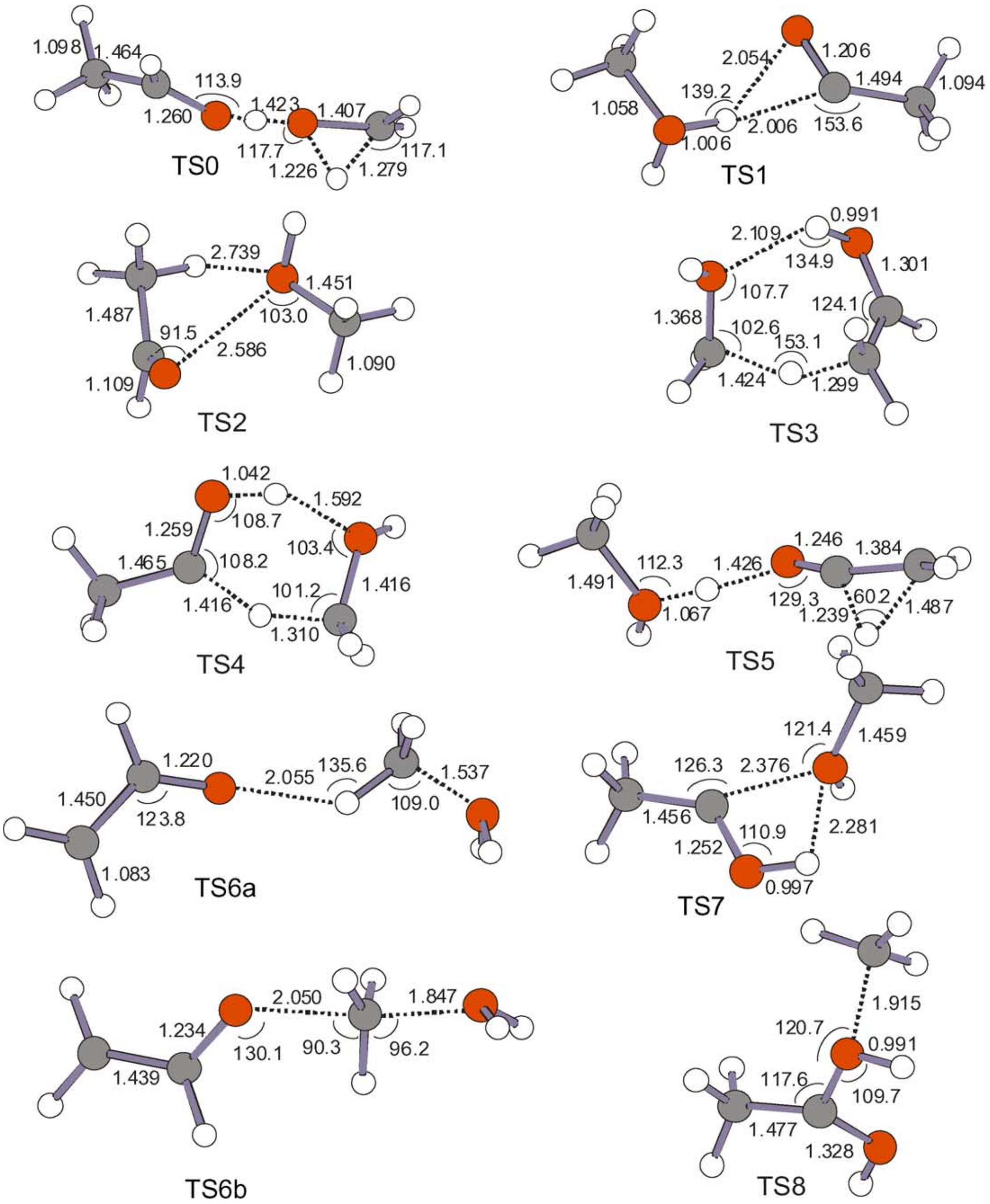


Fig. 6 (b) Optimized geometries of the transition states at MP2/6-31+G(D).

(MECP) at RHF/DZP level which works as the transition state for the interconversion of I and II.

The common dissociation channel on PES **1** and **2** is to form $CH_3OH_2^+$ and $CH_3CO^\bullet$ but it involves different pathways on the two surfaces. Rotation in the transition state TS2 results in the isomerization of II to III, $CH_3C(O)^\bullet\cdots{}^+HOHCH_3$, and further, III converts to its isomer VI by a very flat transition state TS1 that is only about 2 kJ/mol higher than III. The difference between the structures III and VI is that in III, the $CH_3CO^\bullet$ is electrostatically bound to $CH_3OH_2^+$ by a C···H···O bridge, but via a O···H···O bridge in VI. Then from VI, the complex quickly dissociates to the products. As was mentioned in Section 3.2.1 above, VI can rearrange to IV, $CH_3CHO\cdots H^+\cdots O(H)CH_2^\bullet$ but it should be noted that the transition state TS4 (∼145 kJ/mol) for this isomerization is at a higher energy than the dissociation limit of VI (∼101 kJ/mol). Hence, PES 1 and PES 2 do not communicate with each other, although they have a common Stable State VI.

Another transition state energy, TS0, has been calculated, by which complex I, ion **2**, converts to IV, ion **1**. TS0 lies at a rather high energy, about 191 kJ/mol. In the metastable time frame of the mass spectrometer, a reaction requiring such a high relative internal energy is usually not observable.

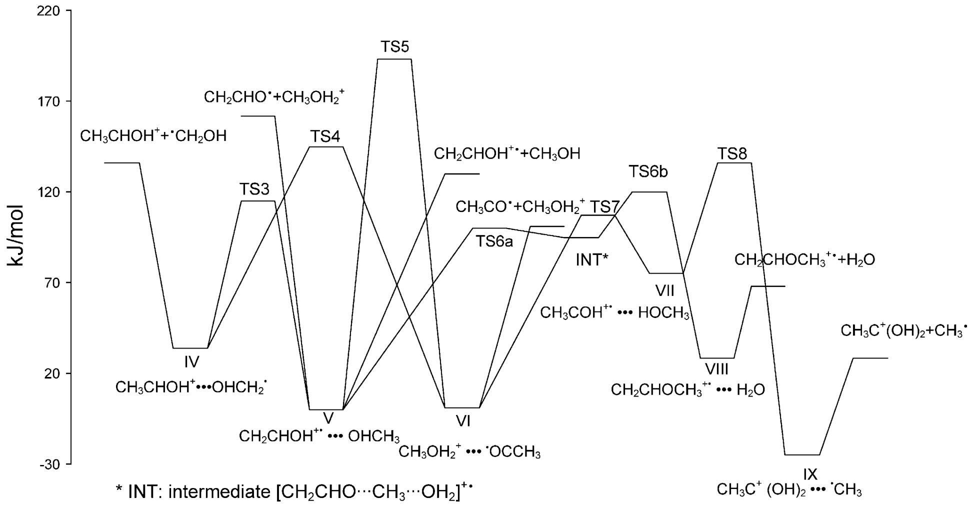


Fig. 7. Potential Energy Surface of $CH_3CHO/CH_2OH_2^{+\bullet}$ system MP2/6-31+G(D).

Again it reflects the experimental observations that the ions **1** and **2** do not have a common chemistry or share the same PES.

3.2.3. Comparison of energy results obtained at different level of theories with experimental data

The relative energies calculated at MP2/6-31+G(D), B3-LYP/6-31+G(D) and G3 level of theories are listed in Table 2. Note that the single point energies obtained at the G3 level of theory and based on the optimized MP2/6-31+G(D) geometries are close to the MP2/6-31+G(D) results (shown in Table 2) and so further G3 calculations were not performed.

In order to compare these calculated values with experimental data, reference values of $\Delta_f H$ for all the products [22] are used and shown in Table 3. In column 5, the values are the heats of formation of the products relative to the sum of the heats of formation of the vinyl alcohol ion and methanol, in row 8. Column 4 lists the calculated relative energies at the MP2/6-31+G(D) level with row 8, column 3 are the G3//B3-LYP results, column 2 gives the B3LYP/6-31+G(D) values. Note that the G3 energies are very close to the current best experimental data, the differences being no more than 5 kJ/mol. Moreover, the MP2 results are very similar to the G3 energies, with differences of only a few kJ/mol except for the relative energy of the pair, $CH_3CO^\bullet + CH_3OH_2^+$: this may be caused by spin contamination for the double bonded radical structure.

In summary, the distonic methanol ion facilitates the isomerization of acetaldehyde into its enol-ion, but the conventional ion does not.

$$CH_3CHO/^{+}H_2OCH_2^\bullet \rightarrow CH_2CHOH^{+\bullet}/OHCH_3 \quad (I)$$

$$CH_3CHO/^{+\bullet}HOCH_3 \not\twoheadrightarrow CH_2CHOH^{+\bullet}/OHCH_3 \quad (II)$$

A distonic ion is a good proton donor and hydrogen atom acceptor. In reaction (I), a proton is given to a keto group and the

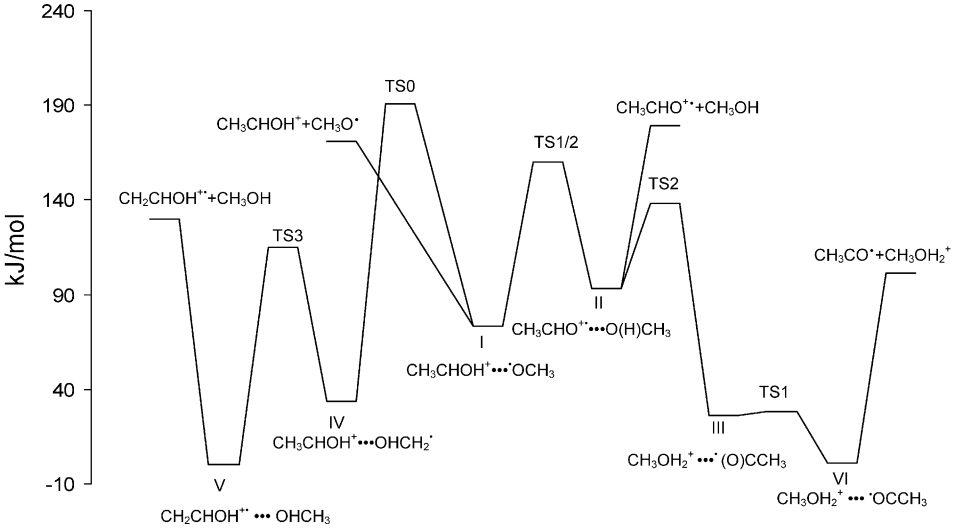


Fig. 8. Potential Energy Surface of $CH_3CHO/CH_3OH^{+\bullet}$ system at MP2/6-31+G(D).

Table 2
Calculated electronic energies (in Hartrees), incorporating a scaled zero-point energy correction, and relative energies (kJ mol^{-1}) at 0 K for the different structures

Structures	B3-LYP/6-31+G(D)		G3//B3-LYP[a]		MP2/6-31+G(D)		G3//MP2[b]	
	E_{cal}	E_{rel}	E_{cal}	E_{rel}	E_{cal}	E_{rel}	E_{cal}	E_{rel}
I	−269.13500	39	−269.01071	65	−268.27967	73		
II	−269.12809	57	−269.00430	82	−268.26842	103		
III	−269.13662	34	−269.02578	25	−268.29778	26	−269.03189	33
IV	−269.13330	43	−269.02846	18	−268.29465	34	−269.03029	37
V	−269.14967	0	−269.03547	0	−268.30751	0	−269.04450	0
VI	−269.14401	15	−269.03367	5	−268.30703	1		
VII	−269.11586	89	−269.00801	72	−268.27899	75		
INT	−269.11605	88	−269.00603	77	−268.27122	95		
VIII	−269.13616	35	−269.02754	21	−268.29688	28		
IX	−269.13749	32	−269.03522	1	−268.31686	−25		
TS0	−269.08149	179	−268.96971	173	−268.23477	191		
TS1	−269.13122	48	−269.02369	31	−268.29704	28		
TS2	−269.13594	91	−268.98352	136	−268.25488	138	−268.99909	119
TS3	−269.12010	78	−269.00121	90	−268.26357	115	−269.00540	103
TS4	−269.10259	124	−268.98845	123	−268.25221	145		
TS5	−269.08189	178	−268.97078	170	−268.23398	193		
TS6a	−269.11497	91	−269.00450	81	−268.26937	100		
TS6b	−269.11112	101	−268.99710	101	−268.26202	120		
TS7	−269.10754	111	−268.99476	107	−268.26676	107		
TS8	−269.10268	123	−268.98750	126	−268.25568	136		

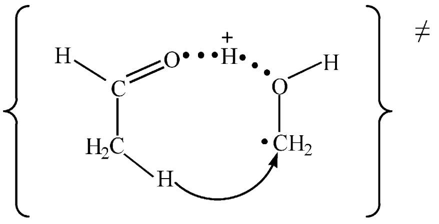
[a] G3//B3-LYP: a single point energy calculation at G3 based on the optimized B3-LYP/6-31+G(D) geometries.

[b] G3//MP2: a single point energy calculation at G3 based on the optimized MP2/6-31+G(D) geometries.

Table 3
Comparison of calculated relative energies (kJ mol^{-1}) with experimental values [22]

Products	B3-LYP/6-31+G(D)	G3//B3-LYP	MP2/6-31+G(D)	Experimental data
$CH_3O^{\bullet} + CH_3CHOH^+$	17	40	41	42
$CH_2OH^{\bullet} + CH_3CHOH^+$	9	3	6	7
$CH_3CO^{\bullet} + CH_3OH_2{}^+$	−4	−9	−29	−7
$CH_3C^+(OH)_2 + CH_3{}^{\bullet}$	−83	−102	−102	−109
$CH_2CHOCH_3{}^{+\bullet} + H_2O$	−55	−62	−62	−68
$CH_3CHO^{+\bullet} + CH_3OH$	36	45	49	50
$CH_2CHOH^{+\bullet} + CH_3OH$	0	0	0	0

radical moiety takes a $H^{\bullet}$ atom back. Thus, the ketone is readily converted to its enol-ion form. The key transition state, TS3 shown below, transfers a $H^{\bullet}$ atom back to the methyl hydroxyl radical undergoing a $H^+/H^{\bullet}$ transfer mechanism.



1,6-H shift TS

4. Conclusions

It has been shown that the stable or metastable ions $[CH_3CHO/{}^{\bullet}CH_2OH_2{}^+]$, **1**, and $[CH_3CHO/CH_3OH^{+\bullet}]$, **2**, have distinct chemistries, i.e., they do not share a common potential energy surface because the transition state connecting them requires too high an internal energy. The two ion–molecule complexes were produced collisionally from appropriate proton-bound pairs and the complex ions have sufficient internal energy to dissociate in the metastable time frame. The important result in the $[CH_3CHO/{}^{\bullet}CH_2OH_2{}^+]$ ion study is that acetaldehyde rearranges to its enol ion. The isomerization is considered to be a new mechanism, a $H^+/H^{\bullet}$ transfer mechanism: after acetaldehyde has accepted a proton from the distonic methanol, the protonated acetaldehyde gives a $H^{\bullet}$ atom back to the ${}^{\bullet}CH_2OH$ radical by a 1,6-H transfer, producing the vinyl alcohol cation attached to a methanol molecule. In contrast, if the acetaldehyde is formally attached to a methanol ion, ion **2**, it cannot access the adjacent $[CH_3CHO/{}^{\bullet}CH_2OH_2{}^+]$ surface. In the former complex, the enol-form ion is not produced, as shown by the isotopic labeling experiments (see Section 3.1.2). This may be due to a higher barrier preventing ion **2** from rearranging to vinyl alcohol ion and methanol, complex V (see Fig. 8). Bimolecular encounters involve higher energies and are able to overcome this high barrier [14], however, the stable or metastable ion–molecule pairs which were made in this study, cannot access this barrier. Instead, ion **2** rearranges to a very stable complex VI and then dissociates to a stable protonated methanol ion and acetyl radical. The theoretical calculations support all the experimental observations. Calculated product energies at MP2/6-31+G(d) and single point energy G3 calculations on optimized geometries at B3-LYP/6-31+G(D) are in good agreement with experimental data.

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