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Gas phase catalyzed keto-enol isomerization of cations by proton transport

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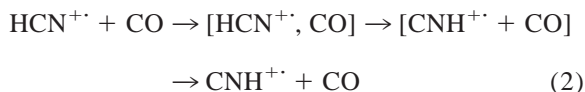
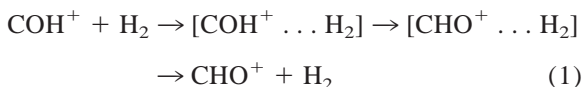
Abstract

In the gas phase, the unimolecular isomerization of the $\text{H}_3\text{COC(O)CH}_2\text{CO}^+$ cation **1** (m/z 101) into the $\text{H}_3\text{CO(HO)CCHCO}^+$ enol ion **2** by a 1,3-H shift possesses a high energy barrier and is therefore not observed. In contrast, in the cell of a FT-ICR mass spectrometer, interaction with gaseous methanol catalyzes the isomerization of **1** into its more stable isomer **2**, which can be characterized by low energy collision with argon. This exothermic reaction is irreversible. Reaction with labeled methanol and ligand exchange experiments indicate the existence of two distinct reactions. By formation of a covalent bond, one reaction yields protonated dimethyl malonate while the second one leads to ion **2** by a 1,3-H transfer catalyzed by methanol. Conversely, loss of methanol from collisionally activated long-lived m/z 133 cations formed by protonation of dimethyl malonate yields some m/z 101 ions with structure **2**, which shows that methanol catalyzes the isomerization of ion **1** within a [**1**, CH_3OH] complex. The efficiency of different catalysts is studied in order to probe the mechanism of the isomerization processes. (Int J Mass Spectrom 179/180 (1998) 293–300) © 1998 Elsevier Science B.V.

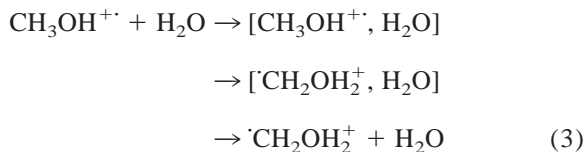
Keywords: Keto-enol isomerization; Catalysis-proton transport; FT-ICR mass spectrometry; Ion-neutral complexes

1. Introduction

In the gas phase, the interaction between an ion and a neutral yields an encounter complex in which reactions can take place. An interesting case occurs when the neutral catalyzes the tautomerization of the neutral within the complex. The occurrence of this “ H^+ -transport” reaction [1] has been demonstrated in several small systems [Eqs. (1) and (2)] [2,3].



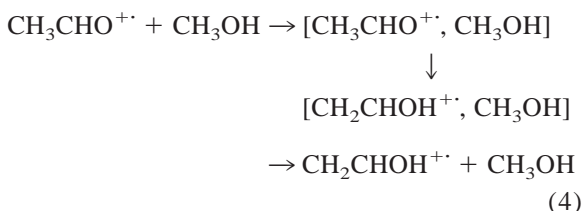
More recently, it has been shown, both by experiment [4] and by calculation [5], that a molecule of water catalyzes the 1,2-H shift which converts ionized methanol CH_3OH^+ into its more stable isomer, the α -distonic ion CH_2OH_2^+ [Eq. (3)]. Similar reactions are observed with $\text{CH}_3\text{CH}_2\text{OH}^+$ [6], CH_3SH^+ [7], and CH_2BrH^+ [4].



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Dedicated to Professor Fulvio Cacace for his outstanding contribution in the field of gas-phase ionic reactions.

Similarly, appropriate neutral molecules catalyze 1,3-H transfers in $\text{ROCH}_2\text{O(H)R}^+$ ions ($\text{R} = \text{H}, \text{CH}_3$) [8,9], and it has been proposed that water can catalyze the isomerization of ionized cyclohexadione into ionized phenol [10]. In a preliminary note [11], it was shown that methanol catalyzes the 1,3-H transfer that converts ionized acetaldehyde into the more stable enol form [Eq. (4)]. It was also suggested that methanol isomerizes the $\text{H}_3\text{COC(O)CH}_2\text{CO}^+$ cation **1**. We report here a detailed experimental study of this process.



2. Experimental

The bimolecular reactions of ions **1** and **2** were studied with a Bruker (Bremen, Germany) CMS-47X FT-ICR mass spectrometer equipped with an external ion source. The neutral reactants were introduced into the cell through a leak valve (Balzers, Lichtenstein) at a pressure of 1×10^{-8} to 4×10^{-8} mbar depending on the experiment, and then diluted with argon, to give a total pressure of 2×10^{-7} mbar. When necessary, a neutral reactant can be introduced by mean of a piezoelectric pulsed valve (Maxtek, Torrance, CA).

The ion–molecule reactions of the ions were examined after isolation and thermalization of the reactant ions formed in the external EI ion source. After transfer into the cell, the ion of interest is first isolated by radio frequency (rf) ejection of all unwanted ions. After a 1.5 s delay, usually sufficient to thermalize the ions by successive collisions with argon, the isolation procedure was repeated by the use of low-voltage single rf pulses (soft shots) at the resonance frequencies of the product ions formed during the relaxation time.

Low energy collision induced dissociation (CID) of ions was performed by applying an on-resonance rf pulse (typically 120 μs irradiation time, $V_{\text{p-p}} = 18 \text{ V}$),

Table 1

Product	ΔE (kcal/mol) ^a
1	12.9
2	0
3	22.7
4	20.5

^a Energies relative to the most stable enol ion **2**, calculated at the B3LYP/6-311+G(3df,2p) including ZPE (see text).

and allowing the excited ions to collide 100–200 ms with the argon bath gas (2.10^{-7} mbar).

Sustained off-resonance irradiation (SORI) [12] was used to excite periodically the ion of interest by applying a long duration off-resonance rf pulse ($V_{\text{p-p}} = 18 \text{ V}$, 1–10 s) in the presence of argon (2.10^{-7} mbar). The maximum kinetic energies brought to the ion (5–25 eV, center of mass values) were chosen to get internal energies of the ion around its dissociation limit.

As previously described [13,14], ion $\text{H}_3\text{COC(O)CH}_2\text{CO}^+$ **1** was formed by loss of a $\text{CH}_3\text{O}^\cdot$ radical from ionized dimethyl malonate while the $\text{H}_3\text{COC(OH)CHCO}^+$ ion **2** was generated by a McLafferty rearrangement from ionized 2-propyl methyl acetoacetate followed by loss of CH_3 . These ions have been shown to be pure.

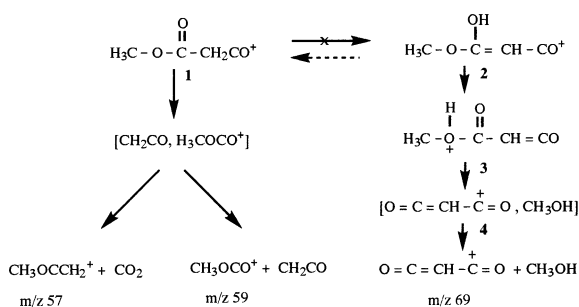
The Gaussian 94 program package was used for calculations [15] to determine the energies of the different possible structures. The geometries were optimized using density functional theory methods, using B3LYP with the 6-31G* basis set, and all structures were checked to be minima on the potential energy surface.

ZPE was computed at this level of the theory, and a single point calculation further performed using the 6-311 + G (3df, 2p) basis set. Table 1 reports the more stable structures found for ions **1** to **4**, although other conformers were found. These results will be presented in another publication.

3. Results and discussion

3.1. Unimolecular reactions of ions 1 and 2

It has been shown [14] that ion $\text{H}_3\text{COC(O)CH}_2\text{CO}^+$ **1** and its enol isomer



$\text{H}_3\text{CO}(\text{OH})\text{CCHCO}^+$ **2** can be selectively generated and distinguished by the unimolecular reactions of the metastable ions (Scheme 1). Metastable ion **1** reacts mainly to give a $\text{CH}_3\text{OCCH}_2^+$ fragment ion (m/z 57; 98%) as well as CH_3OCO^+ ions (m/z 59), whose abundance strongly increases with the internal energy of **1** or upon collision.

The fragmentation of ion **2** begins by two competing 1,3-H transfer processes that involve significant energy barriers and produce hot ions. The first transfer yields **1** and then, by simple cleavage, the m/z 59 fragment ion (20%). The other transfer gives **3** and **4** and then protonated carbon suboxide $\text{C}_3\text{O}_2\text{H}^+$ (m/z 69, 80%) by methanol loss. The absence of m/z 69 fragment in the unimolecular dissociation of **1** shows that the energy barrier for the 1,3-H transfer prevents the unimolecular tautomerization $\mathbf{1} \rightarrow \mathbf{2}$. By contrast, the bimolecular reaction of **1** with methanol causes the complete isomerization of ion **1** into the enol ion **2**.

3.2. Methanol catalyzes the irreversible isomerization of ion 1

When trapped in an FT-ICR cell, ion **1** (m/z 101) fragments upon low energy controlled collision (CID) with argon to yield the characteristic m/z 57 and m/z 59 fragment ions. The same result is obtained when ion **1** is kinetically excited by SORI which confirms that unimolecular isomerization of ion **1** does not take place.

However, when ions **1** (thermalized by collision with 2.10^{-7} mbar of argon for 5 s) were allowed to react with methanol introduced by a pulse valve at

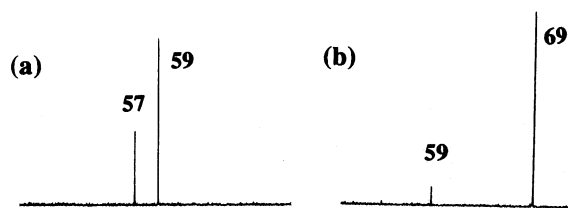


Fig. 1. Low energy CID spectrum of the m/z 101 ions $\text{H}_3\text{COC}(\text{O})\text{CH}_2\text{CO}^+$ **1**, (a) after isolation; (b) after reaction with pulsed methanol.

different pressures (10^{-8} mbar to 5.10^{-7} mbar), the CID spectrum of the m/z 101 ions changes: the m/z 57 ion disappears while a new fragment, m/z 69 ($\text{C}_3\text{O}_2\text{H}^+$, loss of methanol), is observed (Fig. 1).

This clearly demonstrates that methanol catalyzes the isomerization of **1** into one or several more stable ions. Since the low energy CID of the selectively prepared ion **2** leads to both m/z 59 and m/z 69 fragments in a 0.8:10 ratio [16], these isomerized ions are likely to have the structure of the more stable enol ion **2** (Table 1). The formation of minor amounts of ions with structures **3** or **4**, which are intermediates in the unimolecular loss of CH_3OH from **2** (Scheme 1), but whose CID spectra are unknown, cannot a priori be ruled out. However, their energies of formation are calculated to be more than 20 kcal/mol higher than **2** (Table 1).

3.3. Reaction of ion 1 with CH_3OD shows that the isomerization is irreversible

In the presence of CH_3OD , ion **1** exchanges one hydrogen of the CH_2 group. The fact that one hydrogen and just one is completely exchanged, even for long reaction times, shows that methanol catalyzes an irreversible H-transport, isomerizing **1** into **2**, in which one (and just one) hydrogen can be exchanged.

3.4. Reaction of ion 1 with CD_3OH indicates the existence of two pathways

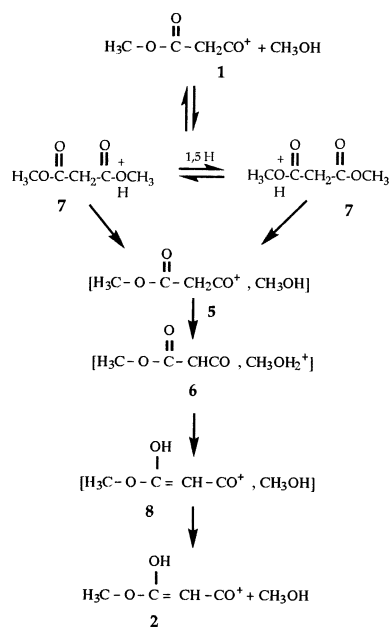
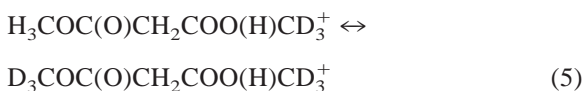
In order to determine the structures of the intermediate(s) and of the final product(s), reactions were performed with CD_3OH . Under these conditions, ion

1 (m/z 101) first reacts rapidly to yield an ion $C_4H_2D_3O_3^+$ m/z 104 but, as the reaction time increases, the abundance ratio $[m/z$ 104] / $[m/z$ 101] reaches an asymptote close to 2. This can be explained by the occurrence of two different reactions.

The first one, corresponding to the remaining unreactive m/z 101 ions, only involves a catalyzed 1,3-H transport and directly yields the enol **2**. This proposal is confirmed by two results. First, the CID spectrum of these m/z 101 ions corresponds to that of the selectively prepared ion **2**. Second, the low reactivity is in agreement with the behaviour of selectively generated ion **2**, which is unreactive towards CD_3OH .

The second pathway corresponds to the formation of m/z 104 ions whose structure depends on the reaction time. After short reaction times ($p = 2 \times 10^{-8}$ mbar, $t = 1$ s), the CID spectrum of m/z 104 ions corresponds mostly to that of ion **1**. In contrast, after long reaction times, the CID spectrum shows two peaks, m/z 62 (CD_3OCO^+) and m/z 69 in the ratio 0.7:10; this corresponds to the CID spectrum of ion **2**. The evolution of the structure of the m/z 104 ions is also illustrated by ligand exchange experiments. These experiments were performed by introducing a constant and low pressure of CH_3OH in the cell and by using pulsed CD_3OH . After short reaction times, the m/z 104 ions undergo a ligand exchange with CH_3OH , as does ion **1**, to yield m/z 101; after long reaction times, the ligand exchange is no longer observed, corresponding to the behaviour of ion **2**.

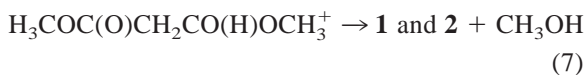
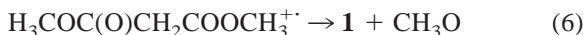
These results suggest that the second reaction involves the formation of a covalent C–O bond giving the protonated dimethyl malonate $H_3COC(O)CH_2COO(H)CD_3^+$. A 1,5-H transfer, from oxygen to oxygen, leads to the isomer ion in which the CH_3 and CD_3 groups are exchanged [Eq. (5)]. Subsequent dissociation yields the $D_3COC(O)CH_2CO^+$ ion, m/z 104, **1**. In further reaction with CD_3OH , this m/z 104 ion undergoes catalyzed isomerization (as does unlabeled ion **1**) to give labeled ion **2**. In order to check this hypothesis, the behaviour of protonated dimethylmalonate was studied.



Scheme 2.

3.5. The catalysis can also be intramolecular

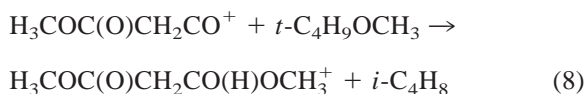
It has been seen that ion **1** (m/z 101) generated in the EI source by cleavage of ionized dimethyl malonate [Eq. (6)] only yields, upon collision, the m/z 57 and m/z 59 fragment ions. The low energy CID of protonated dimethyl malonate **7** (formed in the external source by chemical ionization with isobutane) also leads, as the major fragment, to an ion at m/z 101 (loss of methanol). However, the CID spectrum of this fragment ion shows an abundant peak at m/z 69 (ratio m/z 59: m/z 69 = 4.3). This indicates that, prior to dissociation, a significant proportion of ions **7** rearrange into a [**1**, CH_3OH] complex **5** (Scheme 2) in which the leaving methanol molecule catalyzes the isomerization of ion **1** into ion **2** [Eq. (7)]:



This intramolecular catalysis phenomenon can be enhanced if ions **7** m/z 133 are kinetically excited by sustained off-resonance irradiation (SORI), which offers for CID a softer and more progressive internal energy deposition than on-resonance excitation. The SORI experiments were performed at various maximum kinetic energies (15 to 25 eV, center of mass values). The lower energy was chosen slightly above the dissociation threshold in order to get a sufficient amount of m/z 101 fragment ions to be in turn subjected to CID by on-resonance excitation. In the CID spectra of the ions m/z 101 formed in this way, the ratios m/z 59: m/z 69 decrease from 4.3 to 3.0 (25 eV), 2.3 (20 eV) and 1.6 (15 eV) respectively. Only slight changes in these ratios were observed by varying the time of irradiation.

These results can be interpreted considering that SORI increases the number and/or the lifetime of excited species from ions **7** resembling a [**1**, CH₃OH] complex **5** in which isomerization can occur. However, a majority of the m/z 101 ions retains structure **1**, indicating that the isomerization occurs at energies close to the dissociation threshold, probably through a significant energy barrier [17].

An attempt to generate a long-lived [**1**, CH₃OH] complex was made using the method recently described to prepare monosolvated radical cations by reactions with tert-butanol or tert-butyl methyl ether [18]. Reaction of ion **1** with pulsed tert-butyl methyl ether yields, through elimination of isobutene, a product-ion C₅H₉O₄⁺ m/z 133 corresponding to a net addition to ion **1** of a molecule of methanol. Unfortunately, the reactions of this product ion are those of protonated dimethyl malonate, and therefore the ion may be covalently bonded [Eq. (8)]:



3.6. Mechanism of isomerization can be delineated

These results suggest, in analogy with the reactions previously observed for H⁺ transport [1–10], that the isomerization takes place as indicated in Scheme 2:

- (i) Interaction between ion **1** and methanol leads mainly to the formation of a covalent bond, giving rise to protonated dimethyl malonate H₃COC(O)CH₂COO(H)CD₃⁺ **7**. This ion isomerizes by 1,5-H⁺ transfer [Eq. (5)].
- (ii) The covalent ion rearranges into the complex [H₃COC(O)CH₂CO⁺, CH₃OH] **5** in which the oxygen of CH₃OH is weakly bonded to a methylene hydrogen (Scheme 2).
- (iii) Within **5**, the methanol molecule abstracts a proton from the methylene group to give the stable or transient complex [H₃COC(O)CHCO, CH₃OH₂⁺] **6**, which gives back a proton to the carbonyl group to yield the complex [**2**, CH₃OH] **8**, which is stable [19].

3.7. Reaction of ion **1** with CD₃OD confirms the proposed mechanism

When ion **1** reacts with CD₃OD, the following results are obtained. First, after short reaction times ($t = 0.4$ s, $p = 1.4 \times 10^{-8}$ mbar), only a m/z 104 product appears, demonstrated by CID to possess the structure **1** [Figs. 2 and 3(a)]. Second, at longer times (from 0.5 s up to 2 s), three products are observed: m/z 102 and m/z 105 almost in a 1/1 ratio and m/z 104 in somewhat larger yield [Figs. 2 and 3(b)]. CID spectra show that m/z 102 and m/z 105 possess structure **2** and that m/z 104 is a mixture of structures **1** and **2**. When m/z 104 is continuously ejected, m/z 102 and 105 remain in the same ratio for short to moderate reaction times [Fig. 3(c)], which indicates that they are both primarily formed from the initial reactant and by the same process. Finally, after long reaction times m/z 102 and m/z 105, both with structure **2**, are observed [Fig. 3(d)].

The results confirm the mechanism proposed in scheme 2:

- (i) Interaction between ion **1** and methanol-*d*4 leads mainly to the formation of protonated dimethyl malonate H₃COC(O)CH₂COO(D)CD₃⁺; this reversibly isomerizes into D₃COC(O)CH₂COO(D)CH₃⁺ [Eq. (5)], which explains the product m/z 104 of structure **1** formed at short reaction times. The interconversion of covalently

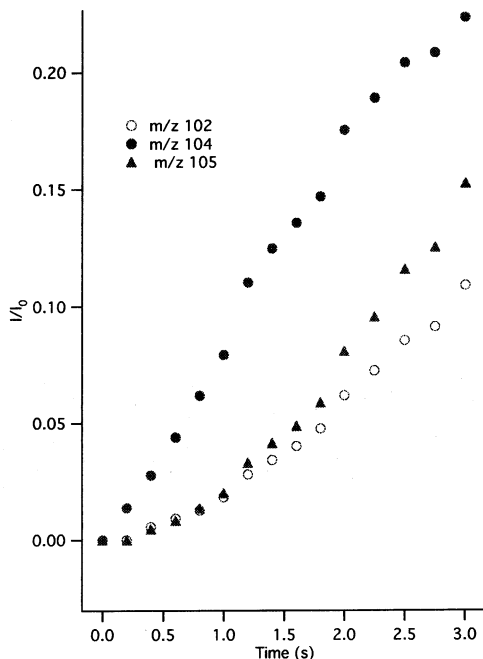


Fig. 2. Reaction of ions $\text{H}_3\text{COC(O)CH}_2\text{CO}^+$ **1** (m/z 101) with CD_3OD (1.4×10^{-8} mbar): plot of relative intensities vs. time (up to 3 s) of the product ions m/z 102, m/z 104, and m/z 105.

bonded ions may precede the formation of the complexes **5** (Scheme 2) [$\text{D}_3\text{C-O-C(O)-CH}_2\text{CO}^+$, CH_3OD] and [$\text{H}_3\text{C-O-C(O)-CH}_2\text{CO}^+$, CD_3OD].

- (ii) This interconversion and the existence of a CH_3OH_2^+ component in the [$\text{H}_3\text{C-O-C(O)-CHCO}$, CH_3OH_2^+] complex **6**, facilitate an exchange of the CH_3 groups as well as of the hydroxylic hydrogen of methanol with one hydrogen of the methylene group. In this way, **7** can eliminate four isotopomers of methanol, CD_3OD , CD_3OH , CH_3OD , and CH_3OH , which lead respectively to m/z 101, m/z 102, m/z 104, and m/z 105 ions with structure **2**. This explains the 1/1 abundance of m/z 102 and m/z 105 for an appreciable span of reaction times, and the higher abundance of m/z 104, which has two origins.
- (iii) For long reaction times allowing several collisions, all the m/z 101 and m/z 104 ions which have the enol structure **2** (CID) exchange their hydroxylic hydrogen [20] to yield, respectively, m/z 102 and m/z 105.

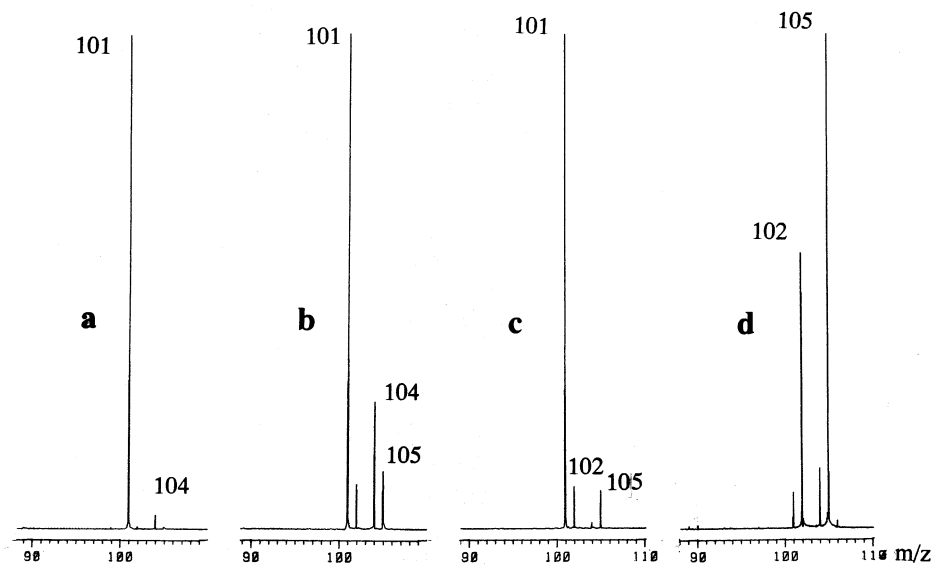


Fig. 3. Reaction of ions $\text{H}_3\text{COC(O)CH}_2\text{CO}^+$ **1** (m/z 101) with CD_3OD (1.4×10^{-8} mbar): (a) reaction time 0.4 s; (b) reaction time 2 s; (c) reaction time 2 s with continuous ejection of m/z 104 ions; (d) reaction time 20 s.

3.8. Other catalysts can be used

For catalyzed isomerization to take place, the catalyst must be basic enough to abstract a proton from the methylene group but not too highly basic, so as to allow the transfer of the proton to the oxygen.

In the presence of water, it is not possible to detect a change in the structure of ion **1** while the long-lived, possibly covalently bonded complex [**1**, H₂O], generated by reaction between **1** and tert-butanol [18], eliminates water upon CID to produce a pure ion **1**. However, using D₂O at a higher pressure ($p = 2 \times 10^{-7}$ mbar), a very slow exchange of one and only one hydrogen is observed ($[m/z\ 102] / [m/z\ 101]$ reaches 0.1 after 5 s) indicating the occurrence of a very slow isomerization. The low efficiency probably arises as a consequence of the low proton affinity of water [21] (PA = 165.2 kcal/mol), preventing it from facile proton abstraction from ion **1**. Experiments with 2,2,2-trifluoroethanol (PA = 167.8 kcal/mol) give rise to a similar conclusion.

In contrast, reactions with formaldehyde (PA = 170.4 kcal/mol), 2-fluoroethanol (PA = 171.0 kcal/mol), formic acid (PA = 177.3 kcal/mol), methanol (PA = 180.3 kcal/mol), methoxyacetonitrile (PA = 181.4 kcal/mol), ethanol (PA = 185.6 kcal/mol) and acetone (PA = 194.1 kcal/mol), result in complete isomerization of **1** into **2**. Finally, in agreement with the mechanism proposed above, reaction with more basic molecules such as ammonia (PA = 204.1 kcal/mol) leads to efficient but irreversible proton transfer.

4. Conclusion

A new example of catalyzed isomerization by proton transport in the gas phase is given in this work. The experiments reported here clearly demonstrate that, within a large interval of proton affinities, a great number of compounds catalyze the 1,3-H⁺ transfer leading to the isomerization of ion **1** into the enol ion **2**.

This mechanism, proposed in scheme 2, is the consequence of at least three factors: greater stability

of ion **2** compared to **1**; strong interaction energy between **1** and methanol in the encounter complex **5** [22], which makes enough excess energy available to pass over the barriers for 1,3-H transfers; role of the catalyst on the transition states, strongly decreasing the energy barriers.

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- [16] This ratio can be taken as a probe for the presence of ions with structure **2** among the m/z 101 ions.
- [17] When the remaining m/z 133 ions after SORI are isolated and subjected to the consecutive CID experiments, their behaviour

is almost identical to that of original ions **7** (m/z 59; m/z 69 = 4). This indicates that only little isomerization, if any, has taken place for the non dissociating m/z 133 ions.

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- [19] In contrast to ion **1**, ion **2** reacts with tert-butyl methyl ether to yield a m/z 133 product ion which undergoes ligand exchange in the presence of CD_3OH . This ion therefore possesses structure [**2**, CH_3OH].
- [20] The rate constant for H/D exchange between **2** and CD_3OD

was found to be one third of the initial rate constant (i.e. for short reaction time) for the reaction between **1** and CD_3OD . Since this rather slow exchange takes place in a consecutive reaction, its contribution must be of minor importance at short reaction times when ion **1** reacts.

- [21] E.P. Hunter and S.G. Lias, J. Phys. Chem. Ref. Data (1997) (to be published). See NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/>).
- [22] For instance, the interaction energy for ionized ethanol and water has been calculated to be about 22 kcal/mol (see [6]).