Catalysed Isomerization of Simple Radical Cations in the Gas Phase

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Interaction with polar neutral molecules can cause α-distonic radical cations and conventional molecular ions to interconvert in the gas phase, in spite of substantial energy barriers for the unassisted isomerization; the interconversion is particularly facile when the proton affinity of the neutral molecule is close to that of the deprotonated radical cation.

A substantial body of experimental and theoretical work has demonstrated that simple, isolated gas-phase α- and β-distonic radical cations and their conventional molecular ion counterparts, do not spontaneously interconvert.[1,2] The energy barriers that separate the isomers have been found by quantum mechanical calculation to be substantial[3] and a variety of methods exists to distinguish experimentally between the isomers.

We have recently observed[4] that $^{\cdot}CH_2OH_2^+$ and $CH_3OH^{\cdot +}$ both exchange all four hydrogens at thermal energies under multiple collision conditions with D_2O in the gas phase, and it was hypothesized that interconversion of the two isomers took place *via* a process involving catalysis by the neutral water molecules. We now report further confirmatory evidence for the mechanism and, furthermore, that such catalysed interconversion appears to be a general phenomenon for α-distonic ions and their molecular ion counterparts. This experimental evidence includes results obtained with sector mass spectrometers as well as with Fourier-transform ion cyclotron resonance (FT-ICR) instruments.[5]

It is well known[6] that the isolated $CH_4O^{\cdot +}$ isomers do not interconvert and that they can be distinguished and characterized by their collision-induced dissociation (CID) reactions. The CID mass spectrum[5] of $CH_3OH^{\cdot +}$ is shown in Fig. 1(*a*). However, when the $CH_3OH^{\cdot +}$ ions are allowed to interact with H_2O prior to analysis, such as when methanol is ionized by electron ionization (EI) in the presence of water at a relatively high pressure (chemical ionization ion source), the CID mass spectrum shown in Fig. 1(*b*) is obtained. This spectrum is characteristic of the $^{\cdot}CH_2OH_2^+$ structure.[7] Clearly, the interaction with H_2O has caused the molecular ions to isomerize to $^{\cdot}CH_2OH_2^+$.

Correspondingly, the bimolecular reactions in the cell of an FT-ICR spectrometer of CH_3OH with $CD_3OH^{\cdot +}$ (formed by EI in an external ion source) result in 1 : 1 transfer of H^+ and D^+ to the neutral methanol; likewise, a 1 : 1 transfer of H^+ and D^+ is observed when $CD_3OD^{\cdot +}$ reacts with CH_3OH. These results show that, prior to proton transfer, the methanol radical cation isomerizes to the α-distonic isomer [eqn. (1)],

$$CD_3OH^{\cdot +} \rightarrow {}^{\cdot}CD_2OHD^+ \qquad (1)$$

a process which is exothermic by 7 kcal mol^{-1} (1 cal = 4.184 J). The isotopic specificity observed with these and related reactant pairs (*e.g.* $CD_3OH^{\cdot +}$ and CD_3OD) when multiple collisions and hydrogen exchange between the reactants have not yet taken place (pressure lower than 5×10^{-8} Torr (1 Torr = 6.66×10^{-6} Pa), time ≤ 1 s) shows that the hydrogen atoms of the neutral reactant are not involved in the proton transfer reactons. This indicates that the isomerization occurs by 1,2-H-migration in the radical cation, not by reciprocal hydrogen transfer between the reactants within the encounter complex.

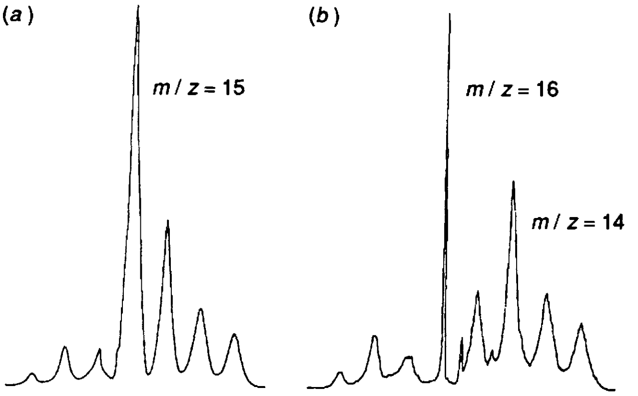

Fig. 1 Partial CID spectra of the *m/z* 32 ions formed: (*a*) by EI of methanol; (*b*) by EI of a water–methanol mixture (10 : 1)

The interconversion appears, nonetheless, to be influenced by the proton affinity of the neutral reaction partner, indicating that the isomerization is aided by the formation of hydrogen bonds or related interactions within the encounter complex. $CH_3OH^{\cdot +}$ and $^{\cdot}CH_2OH_2^+$ undergo virtually identical reactions with neutral molecules whose proton affinity is around or greater than that of $^{\cdot}CH_2OH$ (166 kcal mol^{-1}).[4] However, the reactions with molecules of lower proton affinity can be remarkably different, *e.g.* $^{\cdot}CH_2OH_2^+$ is completely unreactive towards CD_4, whereas $CH_3OH^{\cdot +}$ efficiently abstracts $D^{\cdot}$ to form CH_3OHD^+ (the location of the D on O rather than C was verified by CID).

The ethanol radical cation exhibits similar behaviour, isomerizing in the presence of neutral methanol [eqn. (2)].

$$CH_3CD_2OH^{\cdot +} \rightarrow CH_3{}^{\cdot}CDOHD^+ \qquad (2)$$

The observation that interaction with polar molecules can cause molecular ions to isomerize into their α-distonic counterparts sheds new light on early tandem mass spectrometry experiments. Sieck *et al.*[8] found that $C_2D_5OH^{\cdot +}$ transfers H^+ and D^+ to C_2H_5OH in about a 1 : 1 ratio, and Meisels and coworkers[9] observed that $CD_3OH^{\cdot +}$ transfers H^+ as well as D^+ to acetaldehyde (ratio close to 1 : 1). At the time, these results were taken to show competing proton transfer from C and from O. Correspondingly, McMahon and Beauchamp[10] found in ICR drift cell studies almost identical rates for H^+ and D^+ transfer from $CD_3OH^{\cdot +}$ and $C_2D_5OH^{\cdot +}$ to the corresponding neutral molecules. The same authors observed a 2 : 1 ratio of H^+ and D^+ transfer from $CD_3NH_2^{\cdot +}$ to CD_3NH_2, and a 1 : 1 ratio for H^+ and D^+ transfer from $(CD_3)_2NH^{\cdot +}$. These results suggest that the amine molecular ions also isomerize into their α-distonic counterparts [eqns.

$$CD_3NH_2^{\cdot +} \rightarrow {}^{\cdot}CD_2NH_2D^+ \qquad (3)$$

$$(CD_3)_2NH^{\cdot +} \rightarrow {}^{\cdot}CD_2NHDCD_3^+ \qquad (4)$$

(3) and (4)]. The isotopic specificity observed indicates that the proton-transfer step is more rapid than any re-isomerization to give back the initial molecular ion.[11,12]

The reverse process, isomerization of $^{\cdot}CH_2NH_3^+$ to $CH_3NH_2^{\cdot +}$, is observed in hydrogen atom abstraction reactions with $(CD_3CD_2)_2O$ [eqn. (5)].[13] The collision-induced

$$[{}^{\cdot}CH_2NH_3^+, C_4D_{10}O] \rightarrow [CH_3NH_2^{\cdot +}, C_4D_{10}O] \rightarrow CH_3NH_2D^+ \qquad (5)$$

dissociation of the product $CH_3NH_2D^+$ ions formed from either $CH_5N^{\cdot +}$ reactant shows that the D is located on the nitrogen. Isomerization does not take place when the $CH_5N^{\cdot +}$

isomers react with neutral molecules considerably less basic than $^{\cdot}CH_2NH_2$ (*e.g.* $CH_3NH_2^{\cdot+}$ abstracts H· from C_3H_8 and from CH_3I, $^{\cdot}CH_2NH_3^+$ does not).

The reaction of D_2O with $CH_3Br^{\cdot+}$ as well as with $^{\cdot}CH_2BrH^+$ results in exchange of all three hydrogen atoms. It is interesting that proton transfer to water is not observed with either $CH_3Br^{\cdot+}$ isomer, even though H^+-transfer to H_2O should be considerably exothermic[14] for $^{\cdot}CH_2BrH^+$. This may be explained by the reversible interconversion of [$^{\cdot}CH_2BrH^+$, H_2O], [$CH_3Br^{\cdot+}$, H_2O] and [$^{\cdot}CH_2Br$, H_3O^+] ion-neutral complexes leading to the most stable final products which correspond to ($CH_3Br^{\cdot+}$ + H_2O), not to (H_3O^+ + $^{\cdot}CH_2Br$). Furthermore, both $CH_3Br^{\cdot+}$ isomers transfer CH_3^+ to formaldehyde confirming that $^{\cdot}CH_2BrH^+$ can isomerize to $CH_3Br^{\cdot+}$.

The H/D exchange reaction is also observed for a number of related cations. It is the case for the reactions between D_2O and $CH_3CH_2Br^{\cdot+}$ (2α-H exchanged), D_2O with $CH_3CH_2OH^{\cdot+}$ (3H exchanged), ND_3 with $CH_3NHCH_3^{\cdot+}$ (7H) or CH_3OD with $CH_3OCH_3^{\cdot+}$ (6H).

This shows that the catalysed isomerization of a molecular ion to its α-distonic isomer is a widespread phenomenon. The mechanism appears to bear strong resemblance to what Bohme[15] called 'proton transport catalysis'.

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