The Chemistry of Solvated Distonic Ions: Preparation, Isomerization, and Fragmentation

Ya-Ping Tu[†] **and John L. Holmes***

Contribution from the Department of Chemistry, University of Ottawa, 10 Marie-Curie St., Ottawa, ON K1N 6N5, Canada

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Abstract: It has been shown that solvated distonic ions can be prepared by selected collision-induced radical removal from the proton-bound dimer of appropriate molecules. The α- and β-distonic ethanol ions solvated by methanol or ethanol, $[CH_3{}^{\bullet}CHOH_2{}^{+}/ROH]$ and $[{}^{\bullet}CH_2CH_2OH_2{}^{+}/ROH]$ ($ROH = CH_3OH$ and C_2H_5OH), have been prepared by selected loss of a designated radical from the proton-bound dimer of labeled alcohols, and their reactions studied in the metastable ion time frame. It is found that isomerization of the α-distonic ion to its conventional structure can be catalyzed by both methanol and ethanol, such that the energy barrier to this process is reduced to 25 ± 2 kcal mol^{-1}, lower than that in the uncatalyzed reaction by 10 kcal mo1^{-1}. The β-distonic ions do not isomerize to either the α-form or the conventional form when solvated by the alcohol molecule, and their fragmentation is dominated by water loss, similar to the isolated ion.

Introduction

The chemistry of distonic ions[1,2] has been extensively investigated since their prototype, the distonic methanol ion, was prepared and characterized[3] in 1982. Distonic ions have been identified as stable products[1] or intermediates[4] of the unimolecular fragmentation of gas-phase ions. Although distonic ions are generally more stable than the corresponding molecular ions,[5] these isomers are usually separated by a high energy barrier, and their interconversions do not take place below a dissociation limit of one or another of the species. In 1994, it was reported that the ionization of a simple molecule in the presence of an appropriate compound could directly produce the distonic cation of the molecule; the *m*/*z* 32 ion generated from a mixture of H_2O/CH_3OH (10:1) under chemical ionization conditions showed a collision-induced dissociation (CID) spectrum typical of the ${}^{\bullet}CH_2OH_2{}^{+}$ ion.[6] The water molecule had acted as a catalyst for the interconversion of the $CH_4O^{+\bullet}$ isomers.[7] Subsequent theoretical calculations[8] have found that when the $CH_3X^{+\bullet}$ (X = OH, F, NH_2) ions are associated with a neutral HX molecule, the energy barriers to the isomerization between $CH_3X^{+\bullet}$ and ${}^{\bullet}CH_2XH^{+}$ are substantially decreased.

The catalyzed isomerization of gas-phase ions involving intramolecular proton or carbocation transfer has been studied in many relatively small systems[9−11] and extended recently to some complicated systems.[12−15] The criteria have been defined for choosing the catalyst molecule.[9] For the catalysis to proceed efficiently the proton affinity (PA) of the catalyst molecule should lie between the PA values of the two sites of the substrate molecule. For example, in the $CH_4O^{+\bullet}$ system, the PA of the catalyst should lie between those of the ${}^{\bullet}CH_2OH$ radical at carbon and at oxygen.

In general, the above studies have involved bimolecular encounters between catalyst and ions; in other words, the reactants have been brought together to undergo an exothermic reaction. A more detailed understanding of the catalysis should

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[†] Present address: Department of Research and Development, Apotex Pharmaceutical Company, 400 Ormont Drive, Toronto, Ontario M9L 1T9, Canada.

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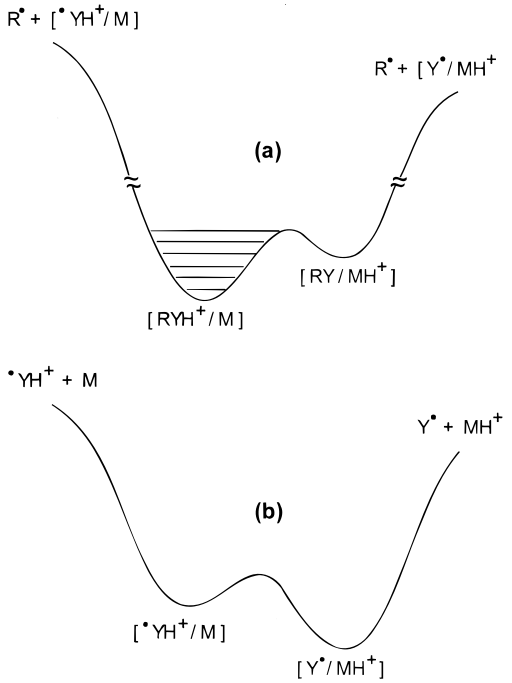

Figure 1. Representative potential energy surfaces for (a) radical loss from the proton-bound dimer of RY and M and (b) isomerization between the solvated distonic ion and the ion-radical complex.

come from examination of the ground-state ion–molecule complex. To do this it is first necessary to devise a method for producing the molecular or distonic ion in association with the catalyst. The generation of an isolated distonic ion usually requires a deliberately designed fragmentation or isomerization of a conventional precursor ion and so it is not straightforward to make a *solvated* distonic ion. Audier et al.[16] have prepared [$^{\bullet}CH_2CH_2O^+(H)CH_3/H_2O$] by reacting the preformed β-distonic ion with *tert*-butyl alcohol using an ion cyclotron resonance instrument. Unfortunately this method has only limited applications in the studies of solvated distonic ions.[17] More recently, we have reported a more widely applicable strategy,[18] which uses collisional activation to remove a designated radical from the proton-bound dimer of two molecules, as exemplified in reaction 1.

$$[RYH^+/M] \rightarrow R^{\bullet} + [^{\bullet}YH^+/M] \tag{1}$$

A simplified potential energy profile (Figure 1a) shows that $R^{\bullet}$ loss from [RYH^+/M] results in the solvated distonic ion, [$^{\bullet}YH^+/M$], whereas $R^{\bullet}$ loss from [RY/MH^+] gives rise to an ion–radical complex, [$^{\bullet}Y/MH^+$]. When the proton affinity of [RY] is greater than that of M, the higher population of stable [RYH^+/M] ions residing in the energy well (the shaded area in Figure 1a) would lead to a greater yield of solvated distonic ions upon collisional activation. However, an inevitable reaction of [$^{\bullet}YH^+/M$] is isomerization to [$^{\bullet}Y/MH^+$], which may only have a trivial energy barrier,[19] irrespective of how the [$^{\bullet}YH^+/M$] ion is initially generated.[16,18] In the bimolecular reactions,[3] where the reactants lie *above* the potential energy surface (rather than within a potential energy well, Figure 1b), association of the distonic ion ($^{\bullet}YH^+$) with the neutral reactant (M) will also produce the ion–radical complex, [$^{\bullet}Y/MH^+$], due to this isomerization.

The α- and β-distonic ethanol ions have been studied extensively,[20–31] especially with regard to their structures. In this paper we describe the metastable reactions of these two distonic ions solvated by methanol or ethanol, [$CH_3{}^{\bullet}CHOH_2{}^+/ROH$] and [$^{\bullet}CH_2CH_2OH_2{}^+/ROH$] (ROH = CH_3OH and C_2H_5OH). The solvated ions were prepared by selected elimination of an H (or D) atom or $CH_3{}^{\bullet}$ from the proton-bound dimers of appropriately labeled alcohols.

Experimental Section

A modified ZAB 3F tandem mass spectrometer[32] with BEE geometry (VG Analytical, Manchester, UK) was used for all experiments. Metastable ion and collision-induced dissociation mass spectra were acquired with the ZABCAT data system[33] by averaging 10–20 consecutive scans, at an accelerating voltage of 8 kV. Helium was used as the collision gas for the CID experiments at a cell pressure of 5×10^{-8} mbar, causing 10–15% attenuation of the main beam.

Proton-bound dimers of alcohols were obtained by introducing individual alcohols through the septum inlet into the CI ion source which was maintained at a temperature of 150 °C and a total pressure of 5×10^{-5} to 1×10^{-4} mbar. The proton-bound dimer was selected by the magnet and subjected to collisional activation in the second field-free region (FFR); the resulting ions were then transmitted to the third FFR, where their unimolecular and CID reactions were observed. Kinetic energy release values were calculated by established procedures[34] using the metastable ion (MI) peak widths at half-height ($w_{0.5}$), which were measured at energy resolution sufficient to reduce the width of the precursor ion main beam to ca. 5 V at half-height.

Labeled methanol, ethanol, and 2-propanol were used to generate isotopomeric solvated distonic ions. Deuterium-labeled compounds (99.9% isotope purity) were purchased from CDN Isotopes (Montreal, QC, Canada) and used without further purification.

Results and Discussion

[$CH_3{}^{\bullet}CHOH_2{}^+/CH_3OH$]. The α-distonic ethanol ion solvated by methanol, **1**, was obtained by collisionally activating the loss of $CH_3{}^{\bullet}$ from 2-propanol or an α-H atom from ethanol, each being proton-bound to methanol as represented in reactions 2 and 3.

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$$[(CH_3)_2CHOD_2^{+}/CD_3OD] \rightarrow [CH_3^{\bullet}CHOD_2^{+}/CD_3OD] + CH_3^{\bullet} \tag{2}$$

$$[CD_3CH_2OD_2^{+}/CD_3OD] \rightarrow [CD_3^{\bullet}CHOD_2^{+}/CD_3OD] + H^{\bullet} \tag{3}$$

To identify the metastable fragmentation products of **1,** three isotopomers, **1**-d_3, **1**-d_6, and **1**-d_9, were prepared and their MI mass spectra are shown in Figure 2. As methyl groups of both the ionic moiety and the neutral methanol were involved in the reactions, ion **1**-d_6 (where one methyl is labeled) and its mass spectrum (Figure 2b) are chosen as a representative. The five reaction channels observed were the losses of $CH_3^{\bullet}$ (of the ion) and $CD_3^{\bullet}$ (of the neutral), losses of ($CH_3^{\bullet} + D_2O$) and ($CD_3^{\bullet} + D_2O$), and the formation of deuteriated methanol. Note that although the losses of (methyl + D_2O) make up more than 50% of the products, loss of water alone was not observed.

Direct loss of $CH_3^{\bullet}$ from either [$CH_3^{\bullet}CHOD_2^{+}/CD_3OD$] or the ion−radical complex, [$CH_3^{\bullet}CHOD/CD_3OD_2^{+}$], would generate a carbene species of high energy and it is therefore unlikely to occur. However, the presence of this loss is most easily rationalized by proposing that isomerization of the α-distonic ethanol ion to the conventional radical cation takes place prior to the $CH_3^{\bullet}$ loss, which produces a proton-bound dimer of formaldehyde and methanol as shown in reaction 4.

$$[CH_3^{\bullet}CHOD_2^{+}/CD_3OD] \rightarrow [CH_3CHDOD^{+\bullet}/CD_3OD] \rightarrow [HDC{=}O\cdots D^{+}\cdots O(D)CD_3] + CH_3^{\bullet} \tag{4}$$

Energetics involved in this reaction will be discussed later; in particular the energy requirement for the isomerization of the distonic ion to the conventional form will be compared with that for the formation of protonated methanol (*m/z* 38 in Figure 2b). The *m/z* 38 ion is formed from the separation of the ion−radical complex, reaction 5.

$$[CH_3^{\bullet}CHOD/CD_3OD_2^{+}] \rightarrow CH_3^{\bullet}CHOD + CD_3OD_2^{+} \tag{5}$$

Loss of the methyl group of methanol (e.g., loss of $CD_3^{\bullet}$ from **1**-d_6 leading to *m/z* 66 in Figure 2b) is proposed to yield the acetaldehyde−water proton-bound dimer as shown in reaction 6.

$$[CH_3^{\bullet}CHOD_2^{+}/CD_3OD] \rightarrow [CH_3CH{=}O\cdots D^{+}\cdots OD_2] + CD_3^{\bullet} \tag{6}$$

This reaction is similar to that in the [$^{\bullet}CH_2OD_2^{+}/CD_3OD$] system studied previously,[18] and is believed to be initiated by attack of the radical of the distonic ion at the oxygen of methanol. This shows the radical property of the distonic ions.

Water loss is a major reaction of the [$^{\bullet}CH_2OD_2^{+}/CD_3OD$] ion,[18] following a mechanism similar to that for the reaction between protonated and neutral methanol.[35−42] However, this reaction was not observed for the distonic ethanol homologue. In contrast, the fragmentation of **1**-d_6 is dominated by losses of ($CH_3^{\bullet} + D_2O$) and ($CD_3^{\bullet} + D_2O$). Is loss of water alone the first step in these two major reactions? The elimination of D_2O from **1**-d_6 would similarly involve isomerization to the ion−radical complex, [$CH_3^{\bullet}CHOD/CD_3OD_2^{+}$], followed by backside displacement leading to a transition state, [$CH_3^{\bullet}CHO(D)\cdots CD_3^{+}\cdots OD_2$]. It has been shown that this transition state has a very high energy relative to the reacting complex.[37,39,42] Therefore, the absence of water loss from **1** indicates that neither ($CH_3^{\bullet} + D_2O$) nor ($CD_3^{\bullet} + D_2O$) loss involves consecutive reactions with loss of water preceding loss of methyl. This is further evidenced by the difference observed in reactions of the ^{18}O-labeled methanol. In the reaction of CH_3OH with $CH_3{}^{18}OH_2^{+}$, losses of H_2O and $H_2{}^{18}O$ with a ratio of 1:3 were found.[35] However, in the fragmentation of the [$CH_3^{\bullet}CHOH_2^{+}/CH_3{}^{18}OH$] ion, *only* [$CH_3^{\bullet} + H_2{}^{18}O$] loss was observed.

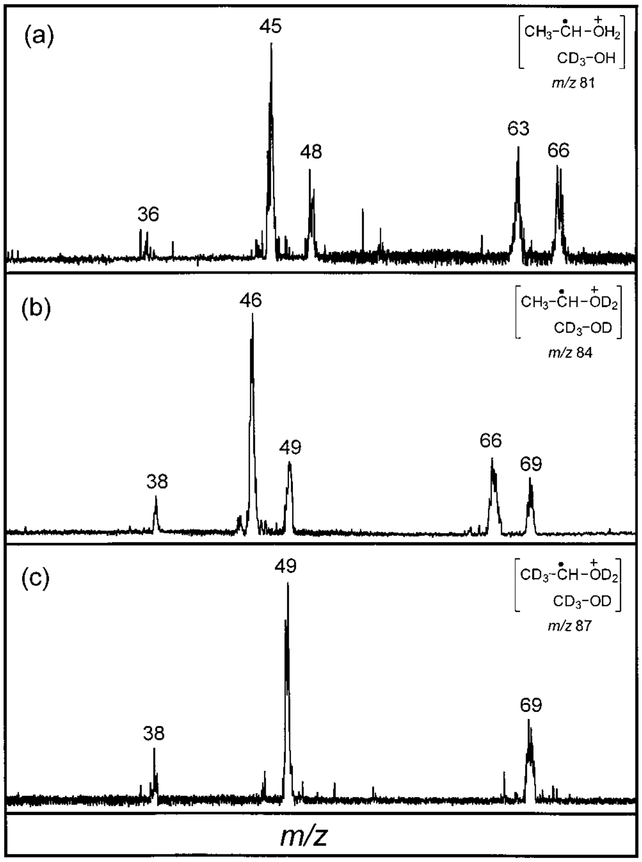

Figure 2. MI mass spectra of the α-distonic ethanol ions solvated by methanol prepared by (a) $CH_3^{\bullet}$ loss from [$(CH_3)_2CHOH_2^{+}/CD_3OH$], (b) $CH_3^{\bullet}$ loss from [$(CH_3)_2CHOD_2^{+}/CD_3OD$], and (c) $H^{\bullet}$ loss from [$CD_3CH_2OD_2^{+}/CD_3OD$].

That the loss of ($CD_3^{\bullet} + D_2O$) is not attributable to simple methyl loss followed by dehydration was shown by probing their CID behavior. Loss of $CD_3^{\bullet}$ alone is *intensified* (rather than decreased) by collisional activation, whereas loss of ($CD_3^{\bullet}$ + D_2O) is completely insensitive to collisions. This result indicates that there is no reaction after $CD_3^{\bullet}$ loss and that this reaction and ($CD_3^{\bullet} + D_2O$) loss should have different transition states. Therefore, an independent pathway leading to loss of ($CD_3^{\bullet} + D_2O$) is proposed; this involves isomerization of **1**-d_6

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to the ion−radical complex, [$CH_3^{\bullet}CHOD/CD_3OD_2^+$], followed by electron transfer between the two partners directly to give the products $CH_3CH{=}OD^+ + CD_3^{\bullet} + D_2O$ as represented in reaction 7. This is in keeping with the low ionization energy of the $CH_3^{\bullet}CHOD$ radical (<6.85 eV)[43] and that the charge transfer (reaction) is exothermic by 4.5 kcal mol^{-1}. In addition, this mechanism is compatible with the observation on the ^{18}O-labeled ions.

$$CH_3^{\bullet}CHOD + CD_3OD_2^+ \rightarrow CH_3CH{=}OD^+ + CD_3^{\bullet} + D_2O \quad (7)$$

$$\Delta H_{rxn} = -4.5 \text{ kcal mol}^{-1}$$

For ($CH_3^{\bullet} + D_2O$) loss, simple $CH_3^{\bullet}$ (reaction 4) and water losses taking place consecutively were excluded by examining the fragmentation of the proton-bound dimer of formaldehyde and methanol (the product ion of reaction 4). Water loss from this dimer (leading to $CH_2{=}O^+CH_3$) is 12.5 kcal mol^{-1} less endothermic than the formation of protonated methanol, but the reaction must have a high energy barrier because the MI mass spectrum is dominated by *m*/*z* 33 and water loss is <1%. Thus we propose a methyl group exchange between the two partners within **1**-d_6, reaction 8, preceding deuteron shift and the subsequent charge transfer (reaction 7) leading to loss of ($CH_3^{\bullet} + D_2O$).

$$[CH_3^{\bullet}CHOD_2^+/CD_3OD] \rightarrow [CD_3^{\bullet}CHOD_2^+/CH_3OD] \quad (8)$$

As stated earlier, isomerization between isolated distonic and conventional ions usually has a high energy barrier; however, when the ion is associated with an appropriate molecule, the reaction is catalyzed and the activation energy is reduced significantly, as has been shown for the methanol ions.[6−8,18] Loss of $CH_3^{\bullet}$ from **1**-d_6 involves isomerization of the distonic ethanol ion to its conventional form (reaction 4). Is this isomerization catalyzed by the solvating methanol?

Although the energy requirement for the isomerization from the α-distonic ethanol ion to ionized ethanol has not been established, it is expected to be similar to that for the methanol ions (32 kcal mol^{-1})[3a,8] and for the dimethyl ether ions (35 kcal mol^{-1})[44] since a 1,2-H shift is required in all these systems. From the fragmentation of the isolated α-distonic ion,[22] the energy barrier to the isomerization can be estimated as follows. The metastable $CH_3^{\bullet}CHOH_2^+$ ion dissociates via three reaction channels, the major being $H^{\bullet}$ loss. This reaction is accompanied by a significant kinetic energy release of 73 meV, compatible with an estimated reverse energy barrier of ca. 20 kcal mol^{-1}. The H atom comes exclusively from oxygen (the $CH_3^{\bullet}CHOD_2^+$ ion loses specifically $D^{\bullet}$), thus the product ion is protonated acetaldehyde.[22] The Δ_fH of $CH_3^{\bullet}CHOH_2^+$ is deduced to be 179.0 kcal mol^{-1} from the Δ_fH[45] and PA (at oxygen)[30] of the $CH_3^{\bullet}CHOH$ radical (Table 1). Therefore, the energy barrier for $H^{\bullet}$ loss is estimated to be 32 kcal mol^{-1}. Another reaction of the distonic ion is $CH_3^{\bullet}$ loss, which takes place after isomerizing to ionized ethanol. As $CH_3^{\bullet}CHOD_2^+$ loses $D^{\bullet}$ only, the isomerization must have an energy barrier of at least 35 kcal mol^{-1} (higher than that for hydrogen atom loss) to prevent H/D exchange.

Table 1. Heats of Formation of Relevant Species

species	Δ_fH (kcal/mol^{-1})	ref
$CH_3^{\bullet}$	34	46
$C_2H_5^{\bullet}$	28	46
$^{\bullet}CH_2OH$	−6	46
CH_3OH	−48	46
C_2H_5OH	−56	46
$CH_3OH_2^+$	137.5	46, 47
$C_2H_5OH_2^+$	124.3	46, 47
$CH_3^{\bullet}CHOH$	−14.5	45
$^{\bullet}CH_2CH_2OH$	−13.5	45
$CH_3^{\bullet}CHOH_2^+$	179.0	21, 30, 45
$^{\bullet}CH_2CH_2OH_2^+$	175.2	3c, 21
$^{\bullet}CH_2CH_2O^+(H)CH_3$	169	estimated[a]
$^{\bullet}CH_2CH_2O^+(H)C_2H_5$	156	estimated[a]

[a] Using Δ_fH for the protonated ether[47] and 101 kcal·mol^{-1} for $D[CH_2{-}H]$.[46]

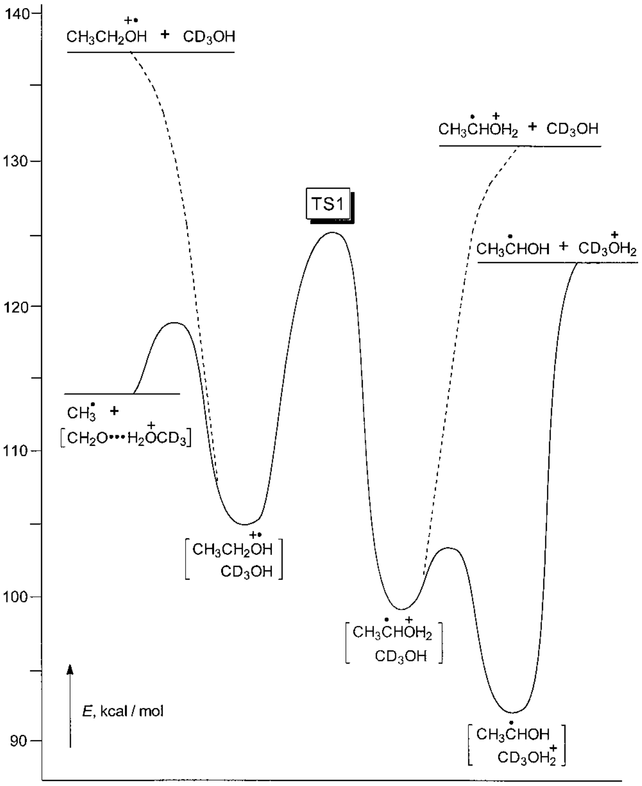

Figure 3. Partial potential energy profile for the fragmentation of the methanol-solvated α-distonic ethanol ion **1**-d_3, [$CH_3^{\bullet}CHOH_2^+/CD_3OH$].

To estimate the activation energy for the interconversion of the ethanol ions in the presence of methanol as a catalyst, a potential energy profile was created as shown in Figure 3 using the thermochemical data[45−47] summarized in Table 1 and using an empirical equation[48] for approximating the energies of proton-bound species. In Figure 3, reaction 4 is compared with the simple separation of the ion−radical complex (reaction 5). As seen clearly in Figure 2b, formation of protonated methanol (*m*/*z* 38) involves no isotope exchange. This indicates that the transition state (TS1) of the interconversion between the two ethanol ions lies higher in energy than the threshold of reaction 5. Considering that the two reactions compared are competing, the energy barrier to the isomerization from distonic to

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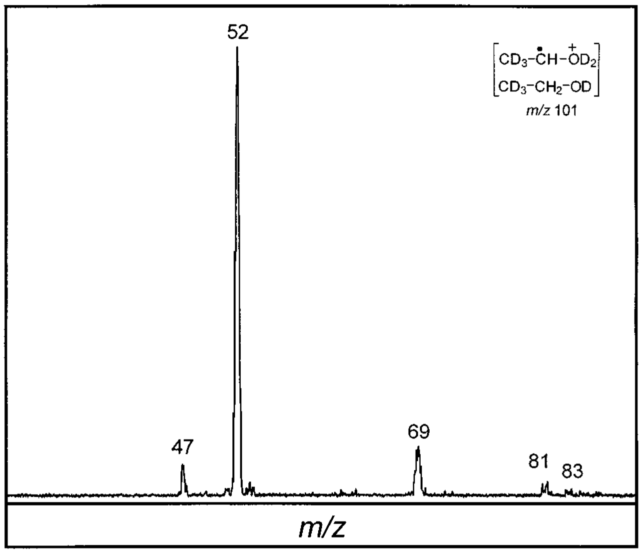

Figure 4. MI mass spectrum of the α-distonic ethanol ion solvated by ethanol obtained by $H^•$ loss from $[CD_3CH_2OD_2^+/CD_3CH_2OD]$.

conventional ethanol ions can be estimated to be 25 ± 2 kcal mol^{-1}. Accurate kinetic energy release values could not be obtained because the signals were too weak at high energy resolution. However, Figure 2b clearly shows that the *m*/*z* 69 peak is broader than *m*/*z* 38, showing that reaction 4 has a larger kinetic energy release than reaction 5. This is in keeping with the proposed energy profile, where TS1 is well above the products of the methyl loss reaction. Now it can be concluded that isomerization of the distonic ethanol ion to ionized ethanol is catalyzed by methanol such that the energy barrier is reduced by 10 kcal mol^{-1}.

Now that catalysis for the interconversion of the ethanol ions is established, a proposal for loss of $CH_3^•$ involving isomerization of $[CH_3^•CHOH/CH_3OH_2^+]$ to $[CH_3CH_2O^•/CH_3OH_2^+]$ followed by the homolytic fission of the ethoxy group can be ruled out. The isomerization of the radical is a 1,2-H atom shift with a high energy barrier. However, the attached $CH_3OH_2^+$ ion cannot interact with the migrating atom to catalyze the reaction.

[$CH_3^•CHOH_2^+/C_2H_5OH$]. The α-distonic ethanol ion solvated by ethanol, **2**, was prepared by collisionally removing an α-H atom from the proton-bound dimer of labeled ethanol, $(CD_3CH_2OD)_2D^+$. The MI mass spectrum of this **2**-*d*$_9$ ion is shown in Figure 4; five products are observed at *m*/*z* 47, 52, 69, 81, and 83. For comparison, another isotopomer, $[CD_3^•CHOH_2^+/CD_3CH_2OH]$, **2**-*d*$_6$, was obtained by $H^•$ loss from $(CD_3CH_2OH)_2H^+$, which shows products at *m*/*z* 46, 50, 66, and 80 with similar abundances.

Loss of $CD_3^•$ from **2**-*d*$_9$ (*m*/*z* 83) is only 1% of the protonated ethanol ion (*m*/*z* 52), much less abundant than observed for ion **1**; its presence, however, implies that isomerization of the distonic ethanol ion to ionized ethanol prior to the elimination does take place (reaction 9).

$$\begin{aligned}[CD_3^•CHOD_2^+/CD_3CH_2OD] &\rightarrow \\ [CD_3CHDOD^{+•}/CD_3CH_2OD] &\rightarrow \\ [HDC{=}O\cdots D^+\cdots O(D)\,CH_2CD_3] + CD_3^• \quad (9)\end{aligned}$$

A potential energy profile similar to Figure 3 may also be constructed by comparing $CD_3^•$ loss with the formation of protonated ethanol. It should be noted that the former is a rearrangement process involving a high-energy transition state, TS1* (as TS1 in Figure 3), whereas the latter is the simple separation of the ion–radical complex, $[CD_3^•CHOD/CD_3CH_2OD_2^+]$. In the metastable ion time frame, such a large difference in product ion abundances indicates that the activation energies of the reactions are at the two extremes of the observable range. The total Δ_fH of $C_2H_5OH_2^+$ and the $CH_3^•CHOH$ radical is 109.8 kcal mol^{-1}; then the energy of TS1* should be ca. 8 ± 2 kcal mol^{-1} higher than this threshold. The $[CH_3^•CHOH_2^+/CH_3CH_2OH]$ ion is estimated to have a Δ_fH of 91 kcal mol^{-1} using 32 kcal mol^{-1} for the proton-binding energy.[39,48] Thus, the energy barrier to the isomerization from $[CH_3^•CHOH_2^+/CH_3CH_2OH]$ to $[CH_3CH_2OH^{+•}/CH_3CH_2OH]$ is expected to be 27 ± 2 kcal mol^{-1}, similar to that in the methanol-catalyzed reaction (Figure 3).

Alternative pathways for $CD_3^•$ loss from **2**-*d*$_9$, which can be ruled out, are to remove $CD_3^•$ from the neutral partner in $[CD_3^•CHOD_2^+/CD_3CH_2OD]$ or from the ionic partner in $[CD_3^•CHOD/CD_3CH_2OD_2^+]$. The product would be $[CD_3^•CHOD_2^+/^•CH_2OD]$ and $[CD_3^•CHOD/^•CH_2OD_2^+]$, respectively, both of which have two radical sites and so would require 40–50 kcal mol^{-1} more energy than reaction 9.

The *m*/*z* 69 ion in Figure 4 is due to loss of $CD_3CH_2^•$ of the neutral partner of **2**-*d*$_9$. This is equivalent to $CD_3^•$ loss from **1**-*d*$_6$ (reaction), and also produces the proton-bound dimer of acetaldehyde and water, $[CD_3CH{=}O\cdots D^+\cdots OD_2]$. The small peak at *m*/*z* 47 in Figure 4 was not identified; it could be $CD_2{=}CHOD^{+•}$ or $CD_3CHO^{+•}$ resulting from deprotonation of the $CD_3^•CHOD$ radical.

It should be noted that for the $C_2H_6O^{+•}$ ions studied here, neither methanol [PA = 180 kcal·mol^{-1}] nor ethanol [PA = 186 kcal·mol^{-1}] has a PA value lying between those of the carbon and oxygen sites in the $CH_3C^•HOH$ and $^•CH_2CH_2OH$ radicals, namely 167, 173 and 178, 168 kcal·mol^{-1}, respectively. The alcohol molecules therefore could not be expected to catalyze the isomerization of the $C_2H_6O^{+•}$ species by the proton transport mechanism. Inspection of the reference data[47] shows few simple molecules which have appropriate proton affinities.

[$^•CH_2CH_2OH_2^+/ROH$] (ROH = CH_3OH and C_2H_5OH). The *β*-distonic ethanol ions solvated by methanol or ethanol, **3** and **4**, were generated from $[CD_3CH_2OH_2^+/CH_3OH]$ and $(CD_3CH_2OH)_2H^+$, respectively, by collision-induced loss of a $D^•$ atom. The MI mass spectra of **3**-*d*$_2$ and **4**-*d*$_5$ are shown in Figure 5. Water loss is the predominant reaction, a remarkable difference from the α-distonic counterparts (see Figures 2 and 4, where water loss is absent or minor). The metastable peak shows a kinetic energy release of 42 and 45 meV for **3**-*d*$_2$ and **4**-*d*$_5$, respectively, and neither is sensitive to collisional activation. Again, the ^{18}O labeled ion $[^•CD_2CH_2OH_2^+/H^{18}OCH_3]$, generated from $[CD_3CHOH_2^+/H^{18}OCH_3]$, produced no surprises, losing only H_2O. Very small peaks at *m*/*z* 48 and 50 attested to minor complex processes.

Clearly, isomerization of the *β*-distonic ion to its α- or conventional isomer is not occurring in either case. This is in accord with the property of the isolated *β*-distonic ion, for which no isomerization was found to occur below its dissociation threshold.[23,24] It is known that the *β*-distonic ethanol ion is well represented as a complex of ionized ethene and water,[20,21,23−26] and that the water loss reaction has an unusually small kinetic energy release (0.2 meV).[26] Therefore, in simple reactions of this ion with many molecules, substitution of water is a significant process.[27−29]

Audier et al.[28] mentioned briefly that in bimolecular reactions of the *β*-distonic ethanol ion with methanol, water loss and proton transfer with a ratio of 100:40 were observed, while in reactions with ethanol, this ratio was 18:100. Kenttamaa[27]

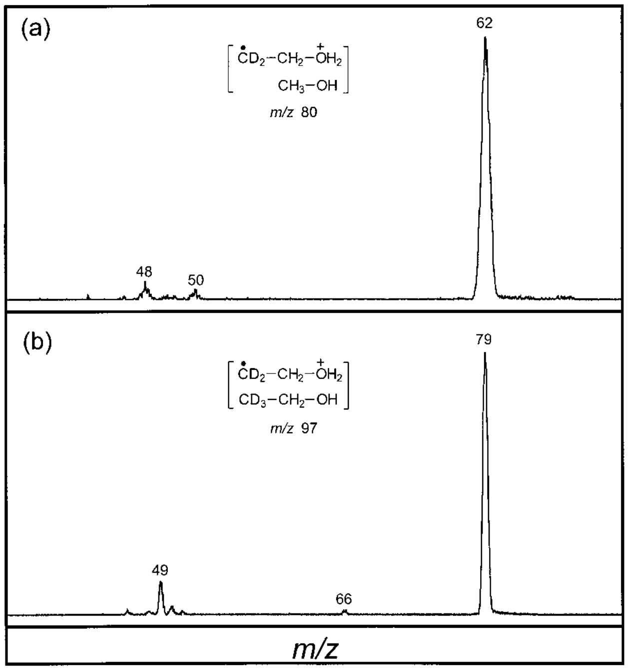

Figure 5. MI mass spectra of the β-distonic ethanol ions solvated by (a) methanol and (b) ethanol prepared by $D^{\bullet}$ loss from the corresponding proton-bound dimers.

reported the reaction of this ion with propanol, where the only channel was proton transfer and water loss did not take place.

The proton affinity of methanol or ethanol (180.5 and 185.7 kcal mol^{-1}, respectively) is lower than that of propanol (188.2 kcal mol^{-1}), but still higher than that of the $^{\bullet}CH_2CH_2OH$ radical at oxygen (177.5 kcal mol^{-1}, cf. Table 1). The lack of proton transfer between the two partners in the solvated ions shows that this reaction cannot compete with water loss. The products of water loss from **3** and **4** are expected to be $^{\bullet}CH_2CH_2O^+(H)R$ ($R = CH_3$, C_2H_5). Using the estimated $\Delta_f H$ values for these two products (Table 1), it is found that water loss is more favorable than proton transfer by ca. 13 and 13 kcal mol^{-1} for ions **3** and **4**, respectively. Theoretical calculations on the thermoneutral reactions of $^{\bullet}CH_2CH_2XH^+$ with XH ($X = OH$, OCH_3, and OC_2H_5) reveal that the reactions follow an S_N2 mechanism where the transition state has a planar α-carbon with two XH molecules on each side,[29] and the central energy barrier increases from $X = OH$ to $X = OC_2H_5$ as shown by the decreasing reaction rate.[29,49] Replacement of water by an alcohol molecule within the solvated ions would involve a similar transition state, the energy of which, however, would be close to the dissociation threshold as indicated by the kinetic energy release value and the CID sensitivity.

Proton transfer observed in bimolecular reactions of this ion with methanol and ethanol[28] clearly reflects that the energy of such reactants therein is higher than that of the metastable adduct ions.

The two small peaks in Figure 5a must arise from complex rearrangements. In Figure 5b, the ion at *m/z* 66 is due to loss of 31 mass units, likely a $^{\bullet}CH_2OH$ radical, producing protonated *n*-propanol. The *m/z* 49 ion could be $^{\bullet}CD_2CH_2OHD^+$, generated from reaction 10.

$$[^{\bullet}CD_2CH_2OH/CD_3CH_2OH_2{}^+] \rightarrow [^{\bullet}CD_2CH_2OH/CD_3CH_2{}^+/H_2O] \rightarrow {}^{\bullet}CD_2CH_2OHD^+ + CD_2CH_2 + H_2O \quad (10)$$

Conclusions

It has been shown that solvated distonic ion $[^{\bullet}YH^+/M]$ can be prepared by removing an $R^{\bullet}$ radical from the proton-bound dimer, $[RYH^+/M]$. The solvated distonic ion can easily isomerize to an ion−radical complex, $[^{\bullet}Y/MH^+]$. Under certain circumstances, isomerization of the distonic ion to its conventional form can be catalyzed by the solvating molecule. The α- and β-distonic ethanol ions solvated with methanol or ethanol, $[CH_3{}^{\bullet}CHOH_2{}^+/ROH]$ and $[^{\bullet}CH_2CH_2OH_2{}^+/ROH]$ ($ROH = CH_3OH$ and C_2H_5OH), were thus prepared and their reactions studied in the metastable ion time frame. It is found that isomerization of the α-distonic ion to its conventional counterpart can be catalyzed by both methanol and ethanol, such that the energy barrier to this process is reduced by 10 kcal mol^{-1} from that for the uncatalyzed reaction. In contrast, the β-distonic ion does not isomerize to any other forms when solvated; its fragmentation is dominated by water loss, similar to the isolated ion.

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