

Selected Radical Removal from Proton-Bound Dimers. A Strategy for Studying Solvated Distonic Ions

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Abstract: The formal ion–molecule pairs [$\bullet\text{CH}_2\text{OH}_2^+/\text{CH}_3\text{OH}$] and [$\bullet\text{CH}_2\text{OH}_2^+/\text{H}_2\text{O}$] were generated by selected radical loss from appropriate proton-bound molecular pairs. The radical loss was activated by keV energy collisions with He in a tandem mass spectrometer, e.g., [$\text{CH}_3\text{CH}_2\text{OD}_2^+/\text{DOCD}_3$] \rightarrow [$\bullet\text{CH}_2\text{OD}_2^+/\text{CD}_3\text{OD}$] + $\text{CH}_3\bullet$. The metastable ion dissociations of the above species and their appropriate deuterium-labeled analogues were recorded. These were the losses of a methyl radical, water, and $\text{C}_2\text{H}_5\text{O}$ from the former pair and losses of water and $\bullet\text{CH}_2\text{OH}$ from the latter. The observations showed that the interconversions of ionized methanol and its distonic isomer were catalyzed by the neutral partner molecule. With H_2O as catalyst, all H atoms are involved in the arrangements that precede metastable dissociations, whereas with methanol as catalyst, its H atoms retain their positional identity. The relationship between these metastable ion systems and the higher energy species involved in bimolecular reaction is discussed in terms of proton-transport catalysis.

Introduction

An early study¹ on the isomerization of radicals, where migration of a group was found to be facilitated by its protonation, resulted *inter alia* in the advent of distonic ions. These unusual radical cations have been extensively investigated² beginning with the first theoretical prediction and successful experimental demonstration of the existence of the distonic methanol ion.³ Distonic ions, which are often thermochemically more stable than their conventional counterparts,⁴ have been shown to be intermediate in many familiar fragmentation reactions of organic ions,⁵ e.g., the McLafferty rearrangement.⁶ More importantly, their ambident properties, stemming from the separation of the radical and charge sites, have created a new dimension in gas-phase ion chemistry.⁷

Isomerization involving hydrogen migration is prevalent among reactions of isolated organic ions in the gas phase, and

such isomerizations often have a large activation energy. However, if such a gas-phase ion is electrostatically bound to (solvated by) an appropriate neutral partner molecule, then the isomerization barrier can be lowered greatly. In the complex, the reaction involving proton transfer is believed to take place in a two-step fashion between the ion and its partner; the process has been termed “proton-transport catalysis”.⁸ A variety of such solvated ions have been explored with the aim of understanding the mechanism of the catalysis.^{9–12}

For distonic ions in particular, a reaction that has attracted considerable attention is their isomerization to the corresponding conventional structure. The prototype distonic ion, $\bullet\text{CH}_2\text{OH}_2^+$, for example, was shown by theory and experiment³ to convert to its radical cation, $\text{CH}_3\text{OH}^{\bullet+}$, but with an energy barrier just above the dissociation limit for $\text{CH}_3\text{OH}^{\bullet+}$ to $\text{CH}_2\text{OH} + \text{H}^{\bullet}$. If a distonic ion is coordinated with an appropriate solvent molecule as described above, proton-transport catalysis should reduce the energy barrier to the isomerization. Recent experimental observations¹³ have shown that the production of the distonic methanol ion is indeed catalyzed by water, and subsequent theoretical calculations^{10a} revealed a substantially decreased energy barrier to the interconversion of the two isomeric methanol ions when water is associated with them. More

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(1) Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 6331–6338.

(2) For a review, see: Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123–202.

(3) (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2929–2930. (b) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2930–2931. (c) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 2931–2932. (d) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *Can. J. Chem.* **1983**, *61*, 2305–2309.

(4) (a) Ma, N. L.; Smith, B. J.; Radom, L. *J. Phys. Chem.* **1992**, *96*, 5804–5807. (b) Gauld, J. W.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 777–784. (c) Gauld, J. W.; Radom, L. *Chem. Phys. Lett.* **1997**, *275*, 28–34. (d) Gauld, J. W.; Holmes, J. L.; Radom, L. *Acta Chem. Scand.* **1997**, *51*, 641–645.

(5) Kentamaa, H. I. *Org. Mass Spectrom.* **1994**, *29*, 1–10.

(6) (a) McAdoo, D. J.; Hudson, C. E. *J. Am. Chem. Soc.* **1981**, *103*, 7710–7713. (b) Osterheld, T. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 2014–2016. (c) Stringer, M. B.; Underwood, D. J.; Bowie, J. H.; Allison, C. E.; Donchi, K. F.; Derrick, P. J. *Org. Mass Spectrom.* **1992**, *27*, 270–276. (d) Bouchoux, G.; Flammang, R.; Jaudon, P.; Lefevre, O. *Org. Mass Spectrom.* **1993**, *28*, 1189–1196.

(7) Stirk, K. M.; Kiminkinen, L. K. M.; Kentamaa, H. I. *Chem. Rev.* **1992**, *92*, 1649–1665.

(8) Böhme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 95–110 and references therein.

(9) (a) Ruttink, P. J. A.; Burgers, P. C. *Org. Mass Spectrom.* **1993**, *28*, 1087–1097. (b) Ruttink, P. J. A.; Burgers, P. C.; Fell, L. M.; Terlouw, J. K. *J. Phys. Chem. A* **1998**, *102*, 2976–2980.

(10) (a) Gauld, J. W.; Audier, H.; Fossey, J.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 6299–6300. (b) Gauld, J. W.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 9831–9839.

(11) (a) Chalk, A. J.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 7573–7578. (b) Chalk, A. J.; Radom, L. *J. Am. Chem. Soc.* **1999**, *121*, 1574–1581.

(12) Trikoupi, M. A.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1998**, *120*, 12131–12132.

(13) (a) Mourgues, P.; Audier, H. E.; Leblanc, D.; Hammerum, S. *Org. Mass Spectrom.* **1993**, *27*, 1098–1100. (b) Audier, H. E.; Leblanc, D.; Mourgues, P.; McMahon, T. B.; Hammerum, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2329–2330.

systematic high-level theoretical calculations^{10b} have been performed on the isomerization of conventional CH_3X^+ ions to their distonic isomers $^{\bullet}\text{CH}_2\text{XH}^+$ for $\text{X} = \text{F}, \text{OH}, \text{and } \text{NH}_2$, supporting the general proposal that interconversion of each ion pair is catalyzed by the corresponding neutral HX molecule.

Generation of a distonic ion requires a carefully selected fragmentation, often involving the isomerization of the chosen conventional precursor molecular ion.² This makes it difficult to prepare a distonic ion that is in association with an appropriate solvent molecule, even by using an ion cyclotron resonance (ICR) instrument¹⁴ which can be used for bimolecular reaction studies of distonic ions.⁷ However, proton-bound dimers are easy to obtain from a chemical ionization (CI) source, and they can be made to lose radical species under collision-induced dissociation (CID) conditions, even though the major metastable ion (MI) reactions are normally cleavages at the proton bridge. Such CID fragmentations could be used to generate solvated distonic ions of interest by selecting the product ion corresponding to loss of a labeled atom or small group. An essential feature for such radical losses in an ion–molecule complex is the existence of a large proton-binding energy between the partners.¹⁵ Reactions of the solvated distonic ions can thus be investigated on a sector mass spectrometer by examining their MI fragmentations, which arise from ions having relatively well-defined energies.

We report here the first experimental observation of the reactions of the distonic methanol ion associated with a neutral methanol molecule, $[\text{CH}_2\text{OH}_2^+/\text{CH}_3\text{OH}]$. The solvated distonic ion and its isotopomers were obtained by selecting products of collision-induced removal of a hydrogen (or deuterium) atom or a CH_3^{\bullet} from the proton-bound dimers of appropriate alcohols, wherein the proton-binding energy between the two hydroxyl groups is about 32 kcal mol⁻¹.¹⁶ Reactions of another solvated ion, $[\text{CH}_2\text{OH}_2^+/\text{H}_2\text{O}]$, were studied in similar fashion.

Experimental Section

All experiments were carried out on a modified¹⁷ ZAB 3F tandem mass spectrometer with BEE geometry (VG Analytical, Manchester, U.K.). Metastable ion and collision-induced dissociation mass spectra were acquired with the ZABCAT program¹⁸ 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, which for these ions causes 10–15% attenuation of the main beam.

Proton-bound dimers of alcohols were generated 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 solvated distonic ions were then transmitted to the third FFR, where their MI and CID reactions were observed. Metastable peak widths ($w_{0.5}$) were determined using sufficient energy resolution to reduce the width of the precursor ion main beam to 5–6 V at half-height; the corresponding kinetic energy release values were calculated by established procedures.¹⁹

CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and $(\text{CH}_3)_2\text{O}$ and CH_3OD , CD_3OH , and CD_3OD were used to generate various isotopomeric solvated distonic ions; the combination for each ion is appropriately given in the discussion of

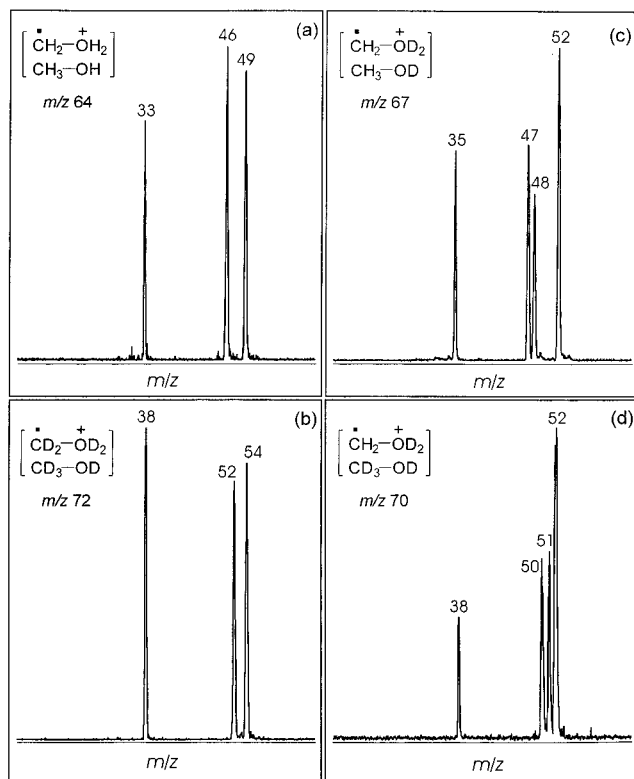


Figure 1. MI mass spectra of the $[\text{CH}_2\text{OH}_2^+/\text{CH}_3\text{OH}]$ ion and its isotopomers generated by collision-induced (a) H^{\bullet} loss from $(\text{CH}_3\text{OH})_2\text{H}^+$, (b) D^{\bullet} loss from $(\text{CD}_3\text{OD})_2\text{D}^+$, (c) H^{\bullet} loss from $(\text{CH}_3\text{OD})_2\text{D}^+$, and (d) CH_3^{\bullet} loss from $[\text{CH}_3\text{CH}_2\text{OD}_2^+/\text{CD}_3\text{OD}]$.

results. Labeled methanols, all of 99.9% isotope purity, were commercially available (CDN Isotopes, Montreal, QC, Canada) and used directly.

Results and Discussion

In the CID mass spectrum of the proton-bound methanol dimer, $(\text{CH}_3\text{OH})_2\text{H}^+$ (m/z 65), the major fragment ions are protonated methanol (m/z 33, 100%) and protonated dimethyl ether (m/z 47, 50%), but a significant signal also arises from the loss of a hydrogen atom (m/z 64, 15%). This latter ion is proposed to be $[\text{CH}_2\text{OH}_2^+/\text{CH}_3\text{OH}]$, **1**, formed by reaction 1; the identity of the hydrogen lost was confirmed by the reaction of isotopomeric dimers, especially $(\text{CH}_3\text{OD})_2\text{D}^+$, for which *only* H^{\bullet} loss was observed (reaction 2).



In the metastable ion time frame the fragmentation of the $[\text{CH}_2\text{OH}_2^+/\text{CH}_3\text{OH}]$ ion proceeds via three channels, namely, the loss of a methyl radical, water elimination, and the formation of protonated methanol, yielding product ions at m/z 49, 46, and 33, respectively, as shown in Figure 1a. The identical fragmentation pattern is obtained for the perdeuterated ion, $[\text{CD}_2\text{OD}_2^+/\text{CD}_3\text{OD}]$, **1-d₈**, as seen in Figure 1b. The intensities of the three product ions are similar, indicating that the three reaction channels have similar activation energies. For the above two isotopomeric solvated ions, carbon and oxygen both carry the same isotopes, and so information on hydrogen exchange between the two sites was not achieved. Therefore, specifically labeled isomers were prepared.

(14) Troude, V.; van der Rest, G.; Mourgues, P.; Audier, H. E. *J. Am. Chem. Soc.* **1997**, *119*, 9287–9288.

(15) Audier, H. E.; Fossey, J.; Mourgues, P.; McMahon, T. B.; Hammerum, S. *J. Phys. Chem.* **1996**, *100*, 18380–18386.

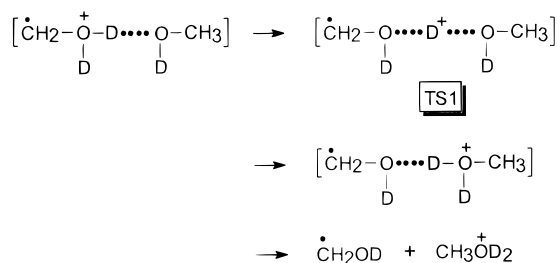
(16) Meot-Ner, M. *J. Am. Chem. Soc.* **1986**, *108*, 6189–6197.

(17) Holmes, J. L.; Mayer, P. M. *J. Phys. Chem.* **1995**, *99*, 1366–1370.

(18) Traeger, J. C.; Mommers, A. A. *Org. Mass Spectrom.* **1987**, *22*, 592–596.

(19) Holmes, J. L.; Terlouw, J. K. *Org. Mass Spectrom.* **1980**, *15*, 383–396.

Scheme 1



The metastable [$\dot{\text{C}}\text{H}_2\text{OD}_2^+/\text{CH}_3\text{OD}$] ion, **1-d₃**, resulting from H \cdot loss from $(\text{CH}_3\text{OD})_2\text{D}^+$ in which all H atoms on O are replaced by D, dissociates such that the peak due to water elimination is split into a pair (m/z 47 and 48, for losses of D₂O and HDO, respectively) while the other two peaks remain as single (m/z 52 for CH₃ \cdot loss and m/z 35 for $\dot{\text{C}}\text{H}_2\text{OD}$ loss, respectively), as shown in Figure 1c. Clearly, generation of CH₃OD₂⁺ (m/z 35) does not involve any H/D exchange between carbon and oxygen atoms prior to dissociation.

The [$\dot{\text{C}}\text{H}_2\text{OH}_2^+/\text{CH}_3\text{OH}$] ion, as shown formally, does not represent the global energy minimum structure on the reaction coordinate (this will be discussed in detail later) but is a proton-bound complex of $\dot{\text{C}}\text{H}_2\text{OH}$ and CH₃OH, which compete for the proton when this ion metastably fragments. The proton affinity (PA) of $\dot{\text{C}}\text{H}_2\text{OH}$ has been determined experimentally^{13a,20} and by theoretical calculations²⁰ to be ca. 166 kcal mol⁻¹ at oxygen and 158 kcal mol⁻¹ at carbon,^{10a} while the PA of methanol²¹ is 180.5 kcal mol⁻¹. Simple proton transfer from the distonic methanol ion, $\dot{\text{C}}\text{H}_2\text{OH}_2^+$, to neutral methanol is exothermic (by ca. 14 kcal mol⁻¹) and leads to [$\dot{\text{C}}\text{H}_2\text{OH}/\text{CH}_3\text{OH}_2^+$], **2**, making the distonic ion an excellent proton donor.

A mechanism is proposed for the generation of CH₃OD₂⁺ (m/z 35) from **1-d₃** (Scheme 1), which involves a formal transition state TS1. As the observation implies, TS1 must be lower in energy than that for the interconversion between the two isomeric CH₄O⁺ ions, so that interconversion between **1-d₃** and the [$\text{CDH}_2\text{OD}^+/\text{CH}_3\text{OD}$] ion, **3-d₃**, is suppressed. Note that it is possible that TS1 may not exist, i.e., the change from the ion molecule pair to ion **2** may be barrier free. This is in good agreement with the conclusions of theoretical studies, which have shown that the energy barrier for proton transfer within a proton-bound complex is quite small, especially when the difference in PA of the two individual molecules is significant.²²

Water elimination from **1-d₃** involves both D₂O and HDO losses with similar abundances (Figure 1c). This can be explained by proposing that hydrogen and deuterium atoms in the distonic moiety are randomized prior to transfer of an H or D atom to the methanol hydroxyl group; the OD (in the HDO and D₂O lost) is *solely* the intact hydroxyl group of the neutral methanol. This requires that, unlike the generation of CH₃OD₂⁺, water elimination has an energy barrier *higher* than that for the isomerization of the distonic methanol ion to its conventional form, a reaction which is a prerequisite for rapid H/D interchange between the carbon and oxygen atoms.

Studies of the reaction of CH₃OH₂⁺ with CH₃OH²³⁻²⁸ have shown that formation of protonated dimethyl ether involves

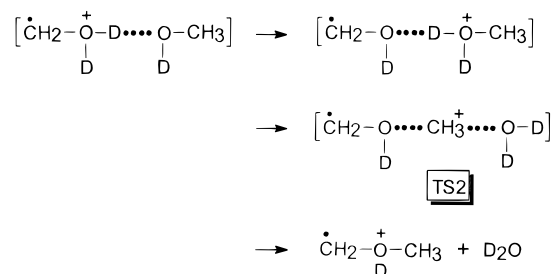
(20) Audier, H. E.; Fossey, J.; Mourgues, P.; Leblanc, D.; Hammerum, S. *Int. J. Mass Spectrom. Ion Processes* **1996**, *157/158*, 275–282.

(21) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413–656.

(22) Scheiner, S. *Acc. Chem. Res.* **1985**, *18*, 174–180 and references therein.

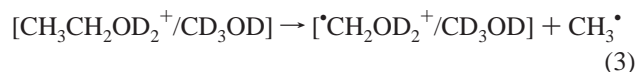
(23) Kleingeld, J. C.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1982**, *17*, 136–139.

Scheme 2

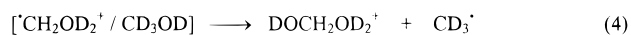


reorientation of the initial proton-bound methanol dimer to [$\text{CH}_3\text{O}(\text{H})\cdots\text{CH}_3-\text{OH}_2^+$], in which backside nucleophilic displacement leads to a transition state, [$\text{CH}_3\text{O}(\text{H})\cdots\text{CH}_3^+\cdots\text{OH}_2$], where a methyl cation is loosely bound with neutral methanol and water on each side. These species are related to the water elimination in a proposed reaction mechanism shown in Scheme 2. Proton transfer from the distonic ion to the neutral methanol is followed by reorientation and subsequent nucleophilic displacement leading to the distonic dimethyl ether ion²⁹ through transition state TS2. The energies for water elimination and protonated methanol formation will be discussed in detail below.

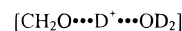
For the methyl radical loss, the MI mass spectra for isotopomers **1**, **1-d₈** and **1-d₃**, shown in Figure 1, panels a–c, respectively, do not indicate which carbon atom is lost. Therefore another isomer, [$\dot{\text{C}}\text{H}_2\text{OD}_2^+/\text{CD}_3\text{OD}$] (**1-d₆**) from [$\text{C}_2\text{H}_5\text{OD}_2^+/\text{CD}_3\text{OD}$], was prepared by removing a CH₃ \cdot radical via collisional activation (reaction 3). The MI mass spectrum of



this ion is shown in Figure 1d, and it confirms the above result that formation of protonated methanol does not involve H/D scrambling, whereas H and D atoms on the ionic partner are completely randomized prior to water elimination. Also, from a comparison of Figure 1, panels a–d, it is apparent that the methyl lost in all cases is from the *original neutral methanol*. This reaction is presumably initiated by attack of $\dot{\text{C}}\text{H}_2$ at the oxygen of the neutral methanol. The formal product ion of this reaction is protonated dihydroxymethane, DOCH₂OD₂⁺, which [if unstable] could rapidly collapse to a proton-bound complex, [$\text{CH}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$], as shown in reaction 4. Due to experi-



↓



mental limitations, it was not possible directly to investigate this formal protonated dihydroxymethane ion. However, in the CID mass spectrum of the (nondeuterated) methanol dimer, an ion having the same elemental composition was observed at m/z 49. It was transmitted to the third FFR, and its CID mass spectrum contained two fragment ions at m/z 19 and 31 with an intensity ratio of 1:10, an observation certainly compatible

(24) Bass, L. M.; Cates, R. D.; Jarrold, M. F.; Kirchner, N. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 7024–7033.

(25) Raghavachari, K.; Chandrasekhar, J.; Burnier, R. C. *J. Am. Chem. Soc.* **1984**, *106*, 3124–3128.

(26) Sheldon, J. C.; Currie, G. J.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 941–944.

(27) Graul, S. T.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 183–202 and references therein.

(28) Bouchoux, G.; Choret, N. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1799–1807.

(29) Bouma, W. J.; Nobes, R. H.; Radom, L. *Org. Mass Spectrom.* **1982**, *17*, 315–317.

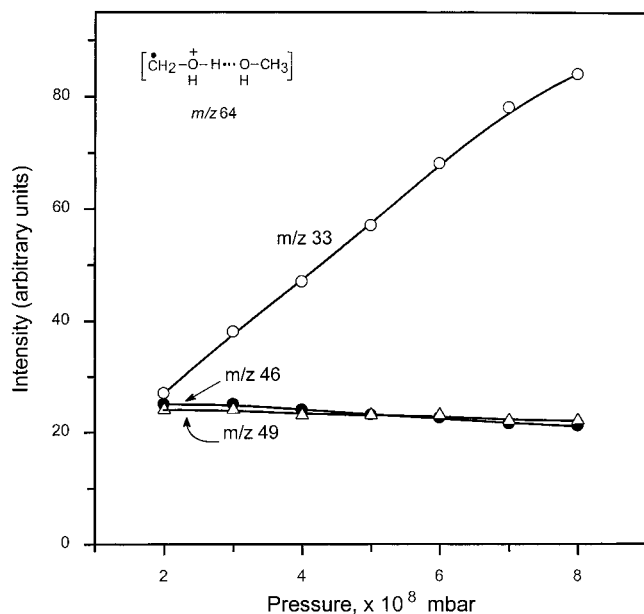


Figure 2. Dependence of the intensity on the pressure of the collision gas (He) in the third FFR for the CID reactions of the $[\text{CH}_2\text{OH}_2^+/\text{CH}_3\text{OH}]$ ion.

with a proton-bound complex of water with formaldehyde, for which the PA values are 165.0 and 170.4 kcal mol⁻¹, respectively.

Distonic ions have been repeatedly shown to have ambident radical and ionic properties. For the systems investigated here, the formation of protonated methanol and water elimination can be attributed to the ionic feature, where competition for a proton is the trigger. In contrast, methyl radical loss is characteristic of the radical nature of the CH_2OH_2^+ ion; indeed, the reaction can be viewed as a radical displacement process.

The three fragmentation channels of ion **1** show substantially different collision characteristics. The losses of $\text{CH}_3\cdot$ and H_2O are *insensitive* to collision while formation of protonated methanol is enhanced significantly thereby. The dependence of the intensity on pressure in the collision cell is given in Figure 2. For a metastable fragmentation to be collision insensitive, the precursor ion must rearrange to a stable isomer via a transition state whose energy is as high as (or even higher than) the dissociation threshold of the new isomer. In keeping with the above reaction mechanisms and the CID results, a potential energy profile was created (Figure 3) for two reaction channels of ion **1**. The energies of the proton-bound complexes at the bottom of the wells are derived from the heats of formation of the products and their binding energy; a common proton-binding energy of 32 kcal mol⁻¹ between two hydroxyl groups^{16,27} was assumed to be appropriate. The energy of ion **3** ($[\text{CH}_3\text{OH}^+/\text{CH}_3\text{OH}]$) is estimated by comparison with the $[\text{CH}_3\text{OH}^+/\text{H}_2\text{O}]$ system.¹⁰ The lower energy isomer of **3**, the $[\text{CH}_3\text{O}^+/\text{CH}_3\text{OH}_2^+]$ ion, **4**, is depicted at an energy higher than that of **1** by the difference in $\Delta_f H^\circ$ of the two radicals, namely, ca. 8 kcal mol⁻¹. Note again that the passage of the ion–molecule pair **3** and **4** to the ground state may not involve an energy barrier. The transition states TS1 and TS2 are positioned to fit the contrasting collision sensitivities and the close competition between the two channels. The location of the barriers is also in keeping with the observed kinetic energy releases. For the water loss reaction, where TS2 is higher in energy than the dissociation threshold of the $[\text{CH}_2(\text{CH}_3)\text{OH}^+\cdots\text{OH}_2]$ complex, $T_{0.5} = 60$ meV; in the formation of protonated methanol, TS1 lies below the threshold,

and here $T_{0.5}$ is only 27 meV. Interconversion of the two isomeric methanol ions should have a transition state TS0 which has an energy between TS2 and the threshold for the formation of protonated methanol. Thus the energy barrier to the isomerization from CH_2OH_2^+ to CH_3OH^+ is estimated to be approximately 17 kcal mol⁻¹, in contrast with 32 kcal mol⁻¹ for the reaction in the isolated ion^{3a,10} and 21 kcal mol⁻¹ for the same reaction when water is involved as the catalyst.¹⁰

From Figure 3, it should be emphasized that, at the energy level for the formation of protonated methanol, H/D positional interchange in the distonic moiety is *not* allowed. However, at the overall energy level for water loss, the interchange occurs rapidly and is expected to be even faster than H^+ or D^+ transfer from the ionic partner to the neutral methanol molecule.

Observation of the reaction starting from appropriately labeled ion **3** should provide support for the proposed energy profile in Figure 3. This reactant pair must first overcome TS0 to isomerize to ion **1**. Such a labeled ion, **3-d₅**, was prepared from the proton-bound methanol–dimethyl ether complex by collisionally removing an ether methyl group as shown in reaction 5. The MI mass spectrum of **3-d₅** is given in Figure 4, in which



the $[\text{CD}_3\text{OD} + \text{H}]^+$ and $[\text{CD}_3\text{OD} + \text{D}]^+$ ions (losses of $\text{C}_2\text{H}_2\text{D}_2\text{O}$ and $\text{C}_2\text{H}_3\text{O}$, respectively) are observed at m/z 37 and 38 with an intensity ratio of 3:1. This result indicates that all the H and D atoms of the CH_3OD^+ ion lose their positional identity, compatible with reversible isomerization of the conventional methanol ion to its distonic form. This is entirely in keeping with both the energy profile and the mechanism for formation of protonated methanol proposed in Scheme 1. Furthermore, Figure 4 also shows that water loss from this species involves HDO and D_2O in a ratio of 3:1 (ions at m/z 50 and 49, respectively), consistent with the dehydration mechanism shown in Scheme 2. Note that m/z 51 corresponds to $\text{CD}_3\cdot$ loss. The two small peaks at m/z 35 and 54 indicate a minor involvement of charge transfer within the ion **3**, after reaction 5 leading to $[\text{CH}_3\text{OD}/\text{CD}_3\text{OD}^+]$; from the latter pair, $[\text{CH}_3\text{OD} + \text{D}]^+$ formation and $\text{CH}_3\cdot$ loss from the neutral molecule, reaction 4, are seen.

Experimental observation^{13b} of the isomerization of the distonic methanol ion catalyzed by water was first carried out such that methanol was allowed to interact with water in a chemical ionization source; the m/z 32 ion thus generated showed CID fragmentation that is characteristic of the distonic isomer. To understand the mechanism underlying this observation, the aqueous ion, $[\text{CH}_2\text{OH}_2^+/\text{H}_2\text{O}]$, was prepared as an isolated species by applying the same procedures as for the methanolated counterpart.

The proton-bound complexes of methanol and water, $[\text{CH}_3\text{OH}_2^+/\text{H}_2\text{O}]$ and $[\text{CH}_3\text{OD}_2^+/\text{D}_2\text{O}]$, were subjected to collisional activation to generate two isotopomeric, hydrated distonic methanol ions via reactions 6 and 7. The MI mass



spectra of these two ions are given in Figure 5, panels a and b, respectively. The nonlabeled ion fragments via two channels: loss of water and loss of $\text{CH}_2\text{OH}\cdot$, producing CH_2OH_2^+ and H_3O^+ , respectively. Collisional activation does not change the intensity of the m/z 32 ion, but protonated water is slightly increased. A third, higher energy channel is generously opened

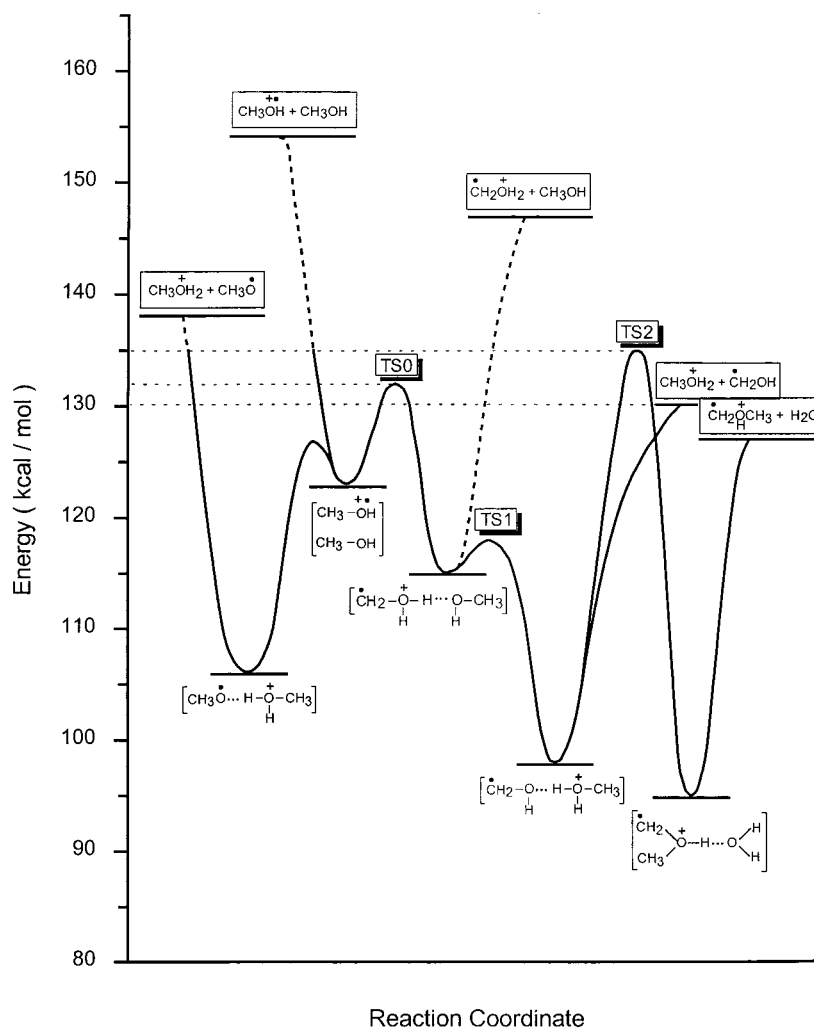


Figure 3. Potential energy profile for the fragmentation of the $[\text{CH}_2\text{OH}_2^+/\text{CH}_3\text{OH}]$ ion. See the text for the details of energies.

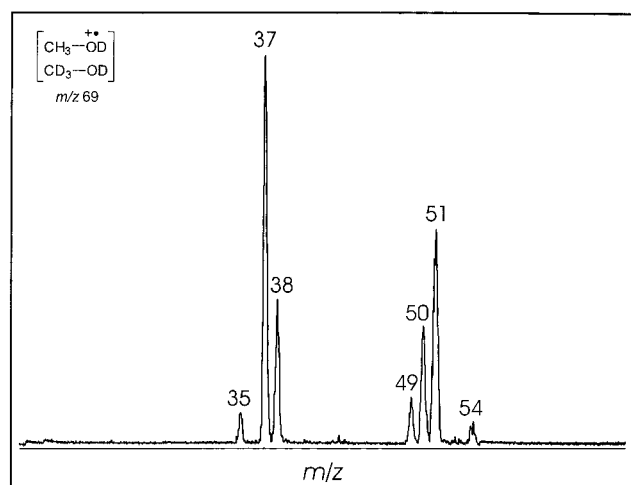


Figure 4. MI mass spectrum of the $[\text{CH}_3\text{OD}^+/\text{CD}_3\text{OD}]$ ion generated by collision-induced CH_3^{\bullet} loss from $[(\text{CH}_3)_2\text{OD}^+/\text{CD}_3\text{OD}]$.

by collision to form protonated methanol. With the $[\text{CH}_2\text{OD}_2^+/\text{D}_2\text{O}]$ ion, isotope interchange is seen from Figure 5b. The peak for water loss becomes three, indicating a different mechanism from that in the methanol–methanol ion system. The intensity ratio observed for losses of D_2O , HDO , and H_2O is close to that calculated (=6:8:1) for complete scrambling of *all* H and D atoms in the system. Note that, unlike the $(\text{CH}_4\text{O})_2^{+\bullet}$ systems,

the alternative ion structures $[\text{CH}_2\text{OH}_2^+/\text{H}_2\text{O}]$ and $[\text{CH}_2\text{OH}/\text{H}_3\text{O}^+]$ are isoenergetic.

In the bimolecular reaction of $\text{CD}_3\text{OH}^{+\bullet}$ with CH_3OH (and other isotopomer pairs) carried out by Audier et al.^{13b} in an ICR instrument, $[\text{CH}_3\text{OH} + \text{D}]^+$ and $[\text{CH}_3\text{OH} + \text{H}]^+$ ions were produced in a 1:1 ratio, but water loss was not mentioned. When the CH_2OH_2^+ ion reacted with D_2O under the same conditions, Audier et al.^{13a} observed rapid exchange of two hydrogen atoms and much slower exchange of the other two hydrogens (of CH_2OH_2^+). However, we have clearly shown that, for both the $[\text{methanol-methanol}]^{+\bullet}$ and $[\text{water-methanol}]^{+\bullet}$ ions, randomization of hydrogen atoms of *only* the ionic partner in the former system and complete randomization of all hydrogen atoms of *both* partners in the latter system were observed in the metastable ion time frame (10^{-6} s). However, it should be recalled that the energy regime for the experiments are significantly different. The bimolecular reactions take place at energies corresponding to the separated pair (see Figure 3) whereas metastable adduct ions are at least 20 kcal mol^{-1} lower in energy. It is thus not surprising that the details of the chemistry are different.

In proton-transport catalysis as in reaction 8, the molecule X transports a proton from site A to site B of the host molecule. This mode of catalysis requires^{8–12} that the proton affinity of the transporter, X, should be greater than the PA of $[\text{A}-\text{B}]$ at A but less than that at B. If the PA of X is significantly greater than that of $[\text{A}-\text{B}]$ at either site, then intermolecular (rather

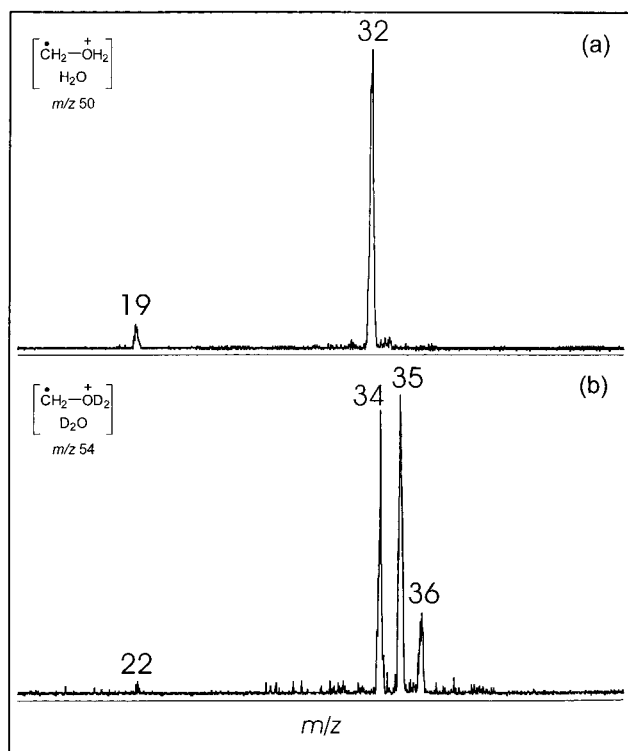
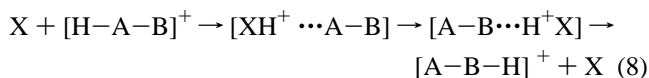


Figure 5. MI mass spectra of (a) [[•]CH₂OH₂⁺/H₂O] and (b) [[•]CH₂OD₂⁺/D₂O] by collision-induced H[•] loss from [CH₃OH₂⁺/H₂O] and [CH₃OD₂⁺/D₂O], respectively.

than intramolecular) proton transfer will be the lower energy process,¹⁰ leading to the formation of the XH⁺ ion as the major product. Thus, for the interconversion of the isomeric CH₄O⁺



ions, water would be the best catalyst since its PA (165 kcal mol⁻¹)²¹ is close to that of [•]CH₂OH at carbon (158 kcal mol⁻¹)^{10a} and at oxygen (166 kcal mol⁻¹).²⁰ In contrast, methanol (PA = 180.5 kcal mol⁻¹)²¹ should not be good.^{13b} Our observations,

however, are to the contrary; the energy barrier to the methanol-catalyzed interconversion is ca. 4 kcal mol⁻¹ lower than that for the water-catalyzed reaction. Therefore, the criterion for choosing an effective catalyst is *not simply the difference in proton affinity of the three appropriate sites*. The difference between H₂O and CH₃OH as catalysts deserves emphasis. For the former case, all the hydrogen atoms of both the ion and the catalyst lose their positional identity before the water loss reaction. For the [methanol⁺/methanol] system, however, all hydrogen atoms of the neutral catalyst molecule *retain* their positional identity prior to the loss of the catalyst. If a formal proton-transport mechanism were involved in the latter case, the transferred proton must always return to the donor ion, i.e., does not exchange even with the OH of the catalyst. We prefer instead to view this catalysis as involving a reversible intraionic 1,2-hydrogen *atom* shift. Detailed high-level theoretical calculations would be required to provide a definitive description of the reaction mechanism.

Conclusions

It has been shown that solvated distonic ions can be prepared by removing a radical from proton-bound dimers under collisional activation conditions and thus their MI and CID reactions can be investigated on a sector mass spectrometer. The solvated distonic ions, in which the two partners interact for an appreciable time as an ion–molecule complex, show pronounced differences in chemical reactivity compared with observations on the (higher energy) bimolecular reactions of the distonic ions with the “solvent” molecules. For the [[•]CH₂OH₂⁺/CH₃OH] ion studied, it was observed that the isomerization of the distonic methanol ion to its conventional counterpart is effectively catalyzed by the neutral methanol molecule. In addition, we have also shown that in so-called proton-transport catalysis, the criterion for choosing a catalyst is not only the difference in proton affinity of the catalyst and the [proton] receptor sites in the radical which lead to the distonic and conventional ions.

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