

Effects of Neutral Bases on the Isomerization of Conventional Radical Cations $\text{CH}_3\text{X}^{\bullet+}$ to Their Distonic Isomers $\bullet\text{CH}_2\text{X}^+\text{H}$ ($\text{X} = \text{F}, \text{OH}, \text{NH}_2$): Proton-Transport Catalysis and Other Mechanisms

James W. Gault and Leo Radom*

Contribution from the Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Received March 11, 1997. Revised Manuscript Received July 25, 1997[⊗]

Abstract: High level ab initio theory is used to investigate the effects of the neutral bases HF, H₂O, and NH₃ on the mechanisms and barriers for isomerization of the conventional radical cations $\text{CH}_3\text{X}^{\bullet+}$ ($\text{X} = \text{F}, \text{OH},$ and NH_2) to their corresponding distonic isomers $\bullet\text{CH}_2\text{X}^+\text{H}$. It is found that the isomerization mechanism is determined largely by the relative proton affinities of the base and the parent radical $\bullet\text{CH}_2\text{X}$. If the proton affinity of the base is substantially lower than the proton affinity at either C or X of $\bullet\text{CH}_2\text{X}$, the barrier is lowered but remains positive relative to separated base plus $\text{CH}_3\text{X}^{\bullet+}$. If the proton affinity of the base lies between that at C and X, the barrier becomes negative and the base successfully catalyzes the isomerization of $\text{CH}_3\text{X}^{\bullet+}$ to $\bullet\text{CH}_2\text{X}^+\text{H}$. In fact, the barrier is found to be negative even in cases where the proton affinity of the base is lower than the lower proton affinity site of $\bullet\text{CH}_2\text{X}$, provided that this proton affinity difference is not too large. If the proton affinity of the base is higher than that at both C and X, the barrier to rearrangement is lowered even further. However, intermolecular proton transfer from the ion to the base rather than intramolecular proton migration is then the lower energy process. An alternative isomerization mechanism for the $[\text{CH}_3\text{OH}/\text{base}]^{\bullet+}$ systems is also detailed in which the base remains bound to the hydroxyl hydrogen throughout. The barriers for this so-called “spectator” mechanism are found to be higher than those for the interconversion of the isolated conventional and distonic ions. A rationalization based on the nature of the intervening ion–base complexes is presented.

Introduction

The chemistry of gas-phase ions is an area of extensive and on-going research. Of particular increasing interest have been the bimolecular reactions of gas-phase ions with neutral molecules. This is due in part to a growing awareness of the importance of ion–molecule interactions. It is often assumed in such studies that the interaction of an ion with a neutral molecule does not alter the nature of the reacting ion, i.e. the ion does not isomerize prior to reaction. Indeed, some bimolecular reactions have been used to distinguish isomeric ions.^{1,2} However, it is increasingly becoming clear that the interconversion of isomeric ions may in fact be catalyzed by their interaction with an appropriate neutral molecule.^{3–8}

As an example of this situation, we consider distonic radical cations, radical cations with spatially separated charge and radical sites.^{1,9} Distonic radical cations, while often thermodynamically more stable than their more conventional counterparts, are usually separated from these isomers by large barriers, enabling the two isomeric forms to be observed independently.^{1,9–13} However, recent experimental⁵ and theoretical⁶ studies have reported a mechanism by which distonic radical cations may interconvert with their conventional ion counterparts through interaction with an appropriate neutral molecule. In particular, these studies showed that the conventional ion $\text{CH}_3\text{OH}^{\bullet+}$ and its distonic isomer $\bullet\text{CH}_2\text{O}^+\text{H}_2$ are able to undergo facile interconversion when allowed to interact with H₂O. The

particular mechanism involved was described as an example of what Bohme⁴ has termed proton-transport catalysis.

The majority of examples of neutral-assisted ion isomerizations to date have concerned proton transfers.^{3–6} However, a recent experimental study⁷ has reported a similar mechanism for the catalyzed transfer of a methyl-cation fragment, i.e. methyl-cation-transfer catalysis, opening up the possibility of

(3) (a) Nobes, R. H.; Radom, L. *Chem. Phys.* **1981**, *60*, 1. (b) Wagner-Redeker, W.; Kemper, P. R.; Jarrold, M. F.; Bowers, M. T. *J. Chem. Phys.* **1985**, *83*, 1121. (c) Freeman, C. G.; Knight, J. S.; Love, J. G.; McEwan, M. J. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *80*, 255. (d) Ruttink, P. J. A. In *The Structure of Small Molecules and Ions*; Naaman, R., Vager, Z., Eds.; Plenum Press: New York, 1988. (e) Ferguson, E. E. *Chem. Phys. Lett.* **1989**, *156*, 319. (f) Bosch, E.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1990**, *112*, 3868. (g) Petrie, S.; Freeman, C. G.; Meot-Ner, M.; McEwan, M. J.; Ferguson, E. E. *J. Am. Chem. Soc.* **1990**, *112*, 7121. (h) Schaftenaar, G.; Postma, R.; Ruttink, P. J. A.; Burgers, P. C.; McGibbon, G. A.; Terlouw, J. K. *Int. J. Mass Spectrom.* **1990**, *100*, 521. (i) Fox, A.; Bohme, D. K. *Chem. Phys. Lett.* **1991**, *187*, 541. (j) Audier, H. E.; Milliet, A.; Leblanc, D.; Morton, T. H. *J. Am. Chem. Soc.* **1992**, *114*, 2020. (k) Ruttink, P. J. A.; Burgers, P. C. *Org. Mass Spectrom.* **1993**, *28*, 1087. (l) Becker, H.; Schröder, D.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116*, 1096. (m) Pereira, A.; Coitiño, E. L.; Ventura, O. N. *J. Mol. Struct. Theochem.* **1994**, *314*, 31. (n) Chou, P. K.; Smith, R. L.; Chyall, L. J.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1995**, *117*, 4374. (o) Ruttink, P. J. A.; Burgers, P. C.; Terlouw, J. K. *Can. J. Chem.* **1996**, *74*, 1078.

(4) Bohme, D. K. *Int. J. Mass Spectrom. Ion Proc.* **1992**, *115*, 95.

(5) (a) Mourgues, P.; Audier, H. E.; Leblanc, D.; Hammerum, S. *Org. Mass Spectrom.* **1993**, *28*, 1098. (b) Audier, H. E.; Leblanc, D.; Mourgues, P.; McMahon, T. B.; Hammerum, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2329. (c) Audier, H. E.; Fossey, J.; Mourgues, P.; McMahon, T. B.; Hammerum, S. *J. Phys. Chem.* **1996**, *100*, 18380.

(6) Gault, J. W.; Audier, H.; Fossey, J.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 6299.

(7) Baranov, V.; Petrie, S.; Bohme, D. K. *J. Am. Chem. Soc.* **1996**, *118*, 4500.

(8) Chalk, A. J.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 7573.

(9) (a) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225.

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1997.

(1) (a) Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649. (b) Kenttämaa, H. I. *Org. Mass Spectrom.* **1994**, *29*, 1.

(2) See, for example: Thoen, K. K.; Beasley, B. J.; Smith, R. L.; Kenttämaa, H. I. *J. Am. Chem. Soc. Mass Spectrom.* **1996**, *7*, 1238 and references therein.

the more widespread occurrence of this phenomenon. It is important to gain a greater understanding of such processes, but we are aware of only one detailed systematic study that has been reported to date, dealing with the catalyzed rearrangement of isoformyl cation to formyl cation.⁸

We have previously published a preliminary report on the effects of H₂O on the isomerization of CH₃OH⁺ to its distonic isomer [•]CH₂O⁺H₂.⁶ In the present article, we broaden our study through an examination of the effects of the neutral bases HF, H₂O, and NH₃ on the mechanism and barrier to isomerization of the conventional ions CH₃F⁺, CH₃OH⁺, and CH₃NH₂⁺ to their distonic isomers [•]CH₂F⁺H, [•]CH₂O⁺H₂, and [•]CH₂N⁺H₃.

Computational Methods

Standard ab initio molecular orbital calculations¹⁴ were performed with the GAUSSIAN 92/DFT^{15a} and GAUSSIAN 94^{15b} suites of programs. Relative energies and other energy data were obtained with a slightly modified G2¹⁶ procedure. The standard G2 method is an approximation procedure that effectively corresponds to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating zero-point vibrational energy (ZPVE) corrections obtained at the (scaled) HF/6-31G(d) level and a higher level correction. We have modified this procedure by using optimized geometries and scaled (by 0.9370)¹⁷ ZPVEs obtained at the second-order Møller–Plesset level employing the frozen-core approximation with the 6-31G(d,p) basis set (MP2(fc)/6-31G(d,p)). These modifications are expected to enable a more accurate determination of geometries and harmonic vibrational frequencies for the types of ions and complexes encountered in the present study. We refer to this modified procedure as G2**.

All relative energies, proton affinities, and other energy data in this paper refer to results obtained at the G2** level at 0 K, unless otherwise noted. Restricted (RMP2) and unrestricted (UMP2) procedures were used for closed- and open-shell species, respectively. The frozen-core approximation (fc) was used throughout. The symbols R, U, and fc have been dropped for brevity.

A potential problem in open-shell calculations that use an unrestricted Hartree–Fock (UHF) reference function is spin contamination. However, in the present study, the extent of spin contamination is small for all the equilibrium structures and for the transition structures for rearrangement. This is reflected in spin-squared expectation values ($\langle S^2 \rangle$) that are all less than 0.8 (compared with 0.75 for a pure doublet). Slightly greater values of $\langle S^2 \rangle$ are found for the transition structures for H[•] loss. Another indication that the results have not been too

adversely affected by spin contamination is that our present results, based on geometries optimized at the UMP2/6-31G(d,p) level, are very close to those that we reported previously for the [CH₃OH/H₂O]⁺ system based on QCISD/6-31G(d,p) optimized structures.⁶

G2** total energies and MP2/6-31G(d,p) optimized geometries (in the form of GAUSSIAN archive files) are presented in Tables S1 and S2, respectively, of the Supporting Information.

Results and Discussion

A. The Isolated Systems. The isomerization of the isolated conventional ions CH₃F⁺ (**1a**), CH₃OH⁺ (**1b**), and CH₃NH₂⁺ (**1c**) to their respective distonic isomers [•]CH₂F⁺H (**2a**), [•]CH₂O⁺H₂ (**2b**), and [•]CH₂N⁺H₃ (**2c**) has been studied in detail previously.^{10d} Our present G2** results are shown schematically in parts a, b, and c of Figure 1 and are in reasonable agreement with previous theoretical values at similarly high levels.^{6,10d–f,11}

Several important points should be noted. In all three systems, the distonic ions (**2a**, **2b**, and **2c**) are more stable than their conventional counterparts (**1a**, **1b**, and **1c**) (by 8.4, 29.5, and 4.6 kJ mol⁻¹, respectively). In addition, for each of the systems there is a large barrier separating the conventional and distonic ions (of 102.0, 108.0, and 155.8 kJ mol⁻¹, respectively). Finally, in all three systems, the lowest energy dissociation of the conventional ions (either directly as for **1a**, or with a barrier as for **1b** and **1c**) requires less energy than that necessary for rearrangement to the distonic isomers. Thus, the conventional ions will preferentially dissociate rather than rearrange to their more stable distonic isomers.

B. The [CH₃F/HF]⁺, [CH₃OH/H₂O]⁺, and [CH₃NH₂/NH₃]⁺ Systems. We begin our investigation of the effect of interaction with a neutral base on the interconversion of conventional and distonic isomers by examining the “fluorine-only” ([CH₃F/HF]⁺), “oxygen-only” ([CH₃OH/H₂O]⁺), and “nitrogen-only” ([CH₃NH₂/NH₃]⁺) systems.

a. [CH₃F/HF]⁺. Our results for the interaction of HF with CH₃F⁺ (**1a**) are shown schematically in Figure 2. When CH₃F⁺ and HF interact they are able to directly form the C–H···FH bound complex **4a** (Figure 2a). Such a complex may also be formed by ionization of a methyl fluoride–hydrogen fluoride dimer or larger cluster. The C–H···FH complex **4a** is able to rearrange to the distonic complex **5a** in two ways (Figure 2a). In the lower energy pathway, HF drags a C–H hydrogen across the C–F bond via the three-membered cyclic transition structure (TS) **6a**, at a cost of 35.0 kJ mol⁻¹, to form **5a**. The second pathway, requiring slightly more energy, 36.5 kJ mol⁻¹, proceeds via the five-membered cyclic TS **7a**. The important difference between these two pathways is that the latter (via TS **7a**) results in an exchange of internal and external protons, i.e. HF gains a C–H proton but loses its original proton in forming the distonic ion, whereas the former (via TS **6a**) does not. It is intriguing that the calculated energy difference between the three- and five-membered cyclic transition structures in this case and in the other transformations considered in this paper is very small and certainly not significant from the point of view of the accuracy of the calculations. In practice, both pathways are probably followed. We note in addition that the three-membered transition structure would be favored by entropy considerations. A similar mechanism of “isomerization by exchange” has been noted previously in the [HO₂/H₂O]⁻ system.^{3f} The scrambling of internal and external protons in the [CH₃F/HF]⁺ system can also be accomplished within **5a** itself via TS **8a** (Figure 2b). This requires approximately 76.0 kJ mol⁻¹, slightly more energy than required for **5a** to exchange protons by interconversion with **4a** (66.7 kJ mol⁻¹).

(10) (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2929. (b) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2930. (c) Radom, L.; Bouma, W. J.; Nobes, R. H.; Yates, B. F. *Pure Appl. Chem.* **1984**, *56*, 1831. (d) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2250. (e) Ma, N. L.; Smith, B. J.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1991**, *113*, 7903. (f) Ma, N. L.; Smith, B. J.; Radom, L. *J. Phys. Chem.* **1992**, *96*, 5804.

(11) Gauld, J. W.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 777.

(12) Schwarz, H. *Shitsuryo Bunseki* **1984**, *32*, 3.

(13) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 2931.

(14) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio molecular orbital theory*; Wiley: New York, 1986.

(15) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92/DFT; Gaussian Inc.: Pittsburgh, PA, 1993. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN 94; Gaussian Inc.: Pittsburgh, PA, 1995.

(16) Curtiss, L. A.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(17) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

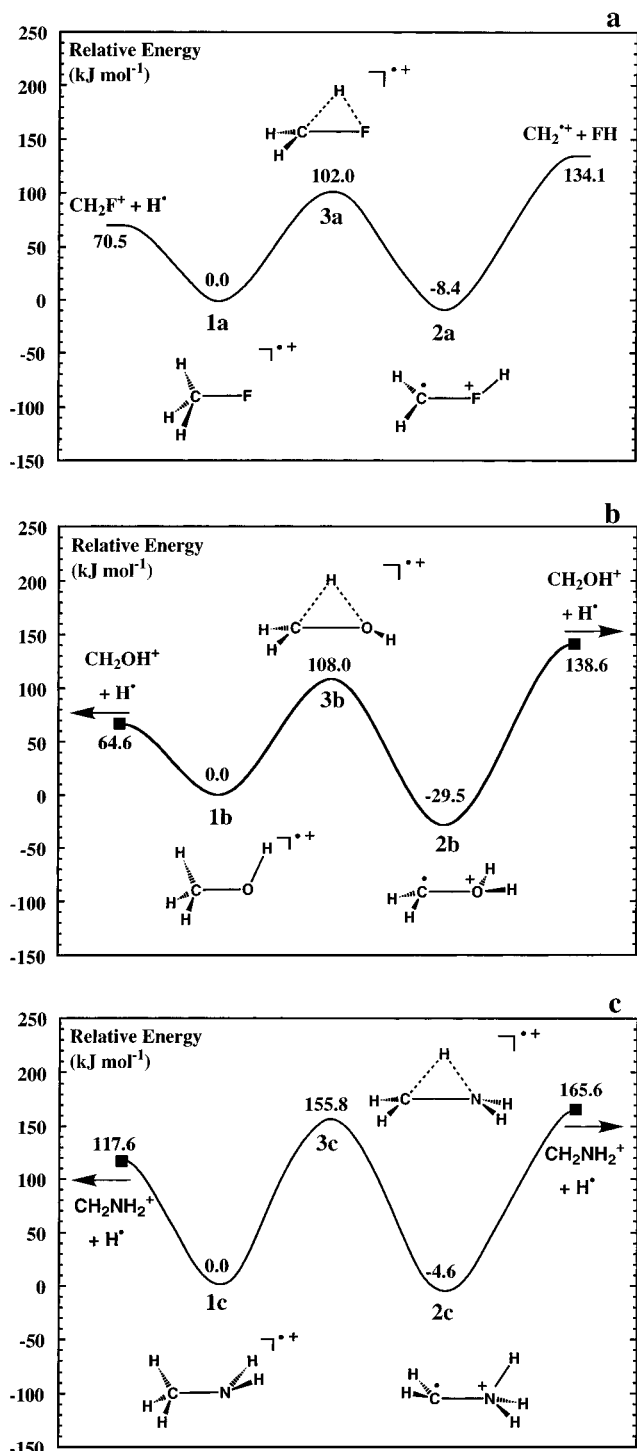


Figure 1. Schematic energy profiles for the interconversion of (a) methyl fluoride radical cation (1a) and the methylenefluoronium radical cation (2a), (b) methanol radical cation (1b) and the methyleneoxonium radical cation (2b), and (c) methylamine radical cation (1c) and the methyleneammonium radical cation (2c) (G2** at 0 K). The ■ symbols represent transition structures for dissociation.

Complexation with HF preferentially stabilizes the distonic radical cation compared with the conventional ion. Thus, 5a lies 30.2 kJ mol^{-1} below 4a (Figure 2a) compared with an energy difference of just 8.4 kJ mol^{-1} between 1a and 2a (Figure 1a).

We note (see Figure 2a) that both TS 6a and TS 7a lie lower in energy than separated $\text{CH}_3\text{F}^+ + \text{HF}$ and $\cdot\text{CH}_2\text{F}^+\text{H} + \text{HF}$, the latter representing the lowest energy dissociation products for 4a or 5a. Thus, the HF molecule has quite effectively catalyzed the isomerization of CH_3F^+ to its distonic isomer,

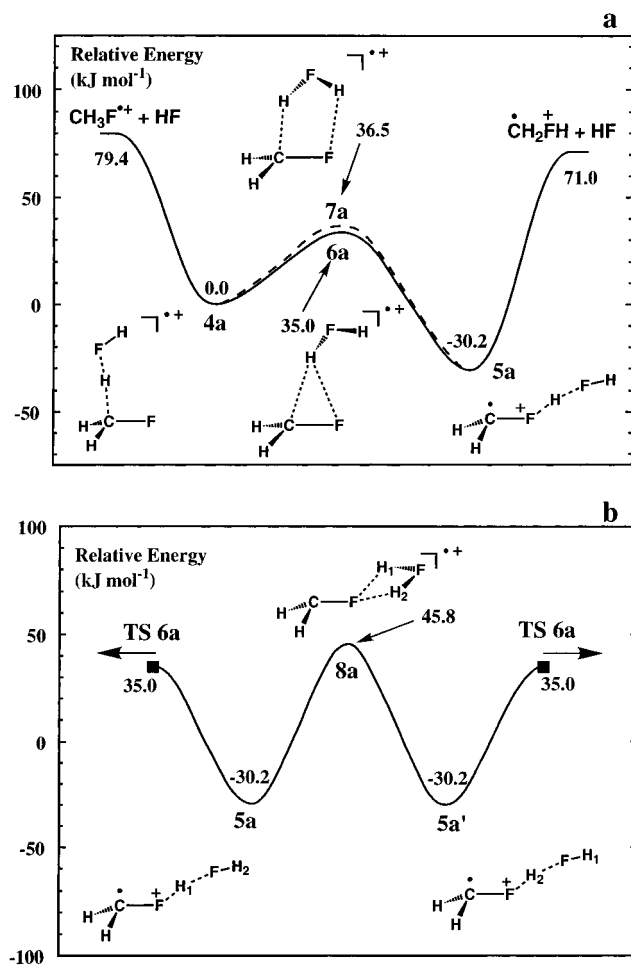


Figure 2. (a) Schematic energy profile for the hydrogen fluoride-catalyzed interconversion of the methyl fluoride and methylenefluoronium radical cations involving the C-H...FH (4a) and F-H...FH (5a) bound complexes. (b) Schematic energy profile for proton exchange between $\cdot\text{CH}_2\text{F}^+\text{H}$ and HF, within 5a (G2** at 0 K).

$\cdot\text{CH}_2\text{F}^+\text{H}$. The mechanism involved is a simple example of proton-transport catalysis.

b. $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^+.$ We have previously published a preliminary report on this system,⁶ but more detailed results are presented here. Interaction of CH_3OH^+ and H_2O can lead directly to the C-H...OH₂ bound complex 4b (Figure 3a), which is analogous to the C-H...FH bound complex 4a (see Figure 2a). There are again two ways by which 4b may rearrange to the distonic complex 5b, requiring very similar energies. The lower energy pathway in this case involves the five-membered cyclic TS 7b, at a cost of 9.5 kJ mol^{-1} , while the higher energy pathway proceeds via the three-membered cyclic TS 6b at a cost of 12.0 kJ mol^{-1} . These pathways are both analogous to those described for the $[\text{CH}_3\text{F}/\text{HF}]^+$ system involving TS 7a and TS 6a, respectively (see Figure 2a). Again, the important difference between the two pathways is that the former (via TS 7b) results in an exchange of internal and external protons, whereas the latter (via TS 6b) does not.

The lowest energy dissociation mechanism for the $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^+$ system is shown in Figure 3b. An intriguing observation from Figure 3b is that the C-H...OH₂ complex (4b) and the O-H...OH₂ complex (9b) have very similar energies. The lowest energy dissociation takes place via the hydrated methanol radical cation (9b) and yields $\text{CH}_2\text{OH}\cdots\text{OH}_2^+ + \text{H}^+$ via a transition structure lying 71.9 kJ mol^{-1} above 4b. Alternatively, starting from 4b would require an initial rearrangement via TS 10b requiring 52.8 kJ mol^{-1} . Both TS 6b and TS 7b lie lower

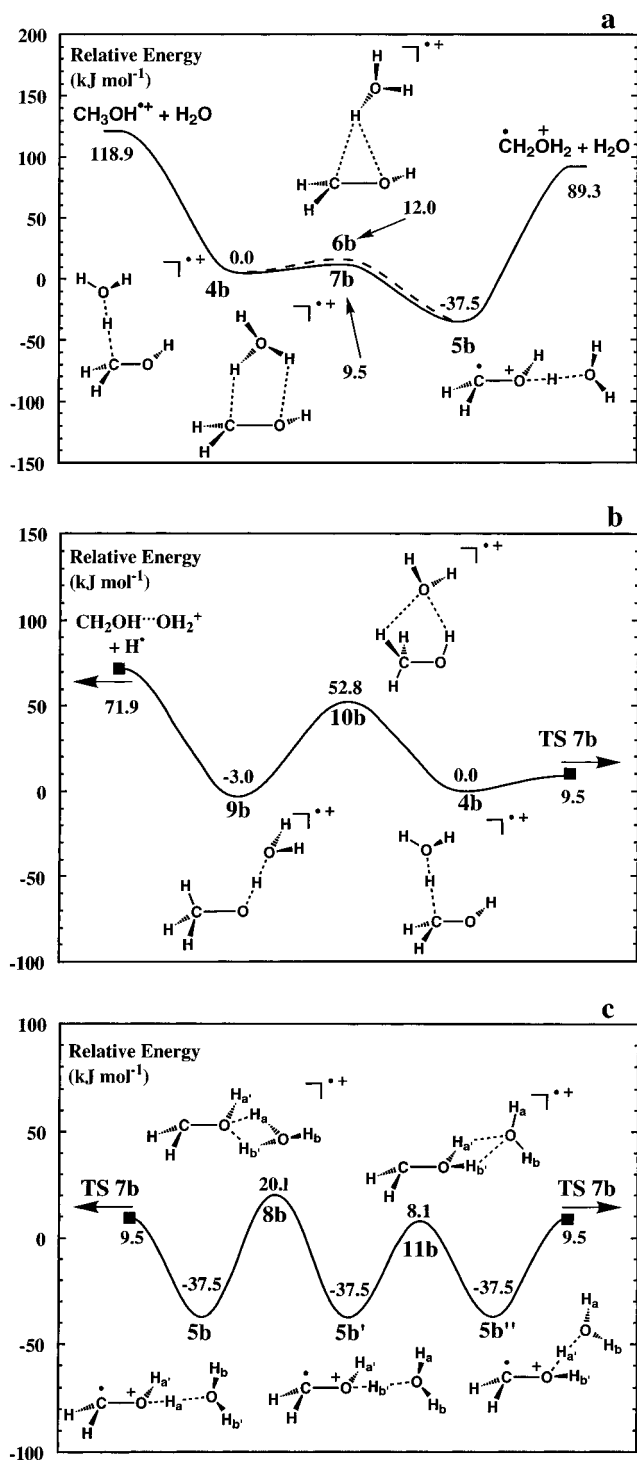


Figure 3. (a) Schematic energy profile for the water-catalyzed interconversion of the methanol and methylenioxonium radical cations involving the C–H···OH₂⁺ (**4b**) and O–H···OH₂⁺ (**5b**) bound complexes. (b) Schematic energy profile for interconversion of the C–H (**4b**) and O–H (**9b**) hydrated forms of the methanol radical cation. (c) Schematic energy profile for proton exchange between [•]CH₂O⁺H₂ and H₂O and for the movement of H₂O between the oxygen-bound protons of **5b** (G2** at 0 K).

in energy than separated [•]CH₂O⁺H₂ + H₂O (89.3 kJ mol⁻¹) or the transition structure for dissociation to CH₂OH···OH₂⁺ + H[•] (71.9 kJ mol⁻¹). Rearrangement therefore takes place preferentially to dissociation. Thus, H₂O has very effectively catalyzed the isomerization of CH₃OH^{•+} to its distonic isomer [•]CH₂O⁺H₂ in another example of proton-transport catalysis.

Deuterium labeling experiments^{5a,5b} show that two of the four protons of CH₃OH^{•+} exchange rapidly with D₂O, while the

remaining two exchange more slowly. The mechanisms detailed in Figure 3 provide a straightforward rationalization for these observations (see also ref 6). We have seen that **4b** may easily isomerize to the distonic ion **5b** via TS **7b**, resulting in the exchange of one C–H proton with a proton of the water molecule (Figure 3a). From Figure 3c, we can see that the migration of H₂O between the oxygen-bound protons of **5b** via TS **11b** costs 45.6 kJ mol⁻¹. In addition, the exchange of protons between the water and distonic ion via TS **8b** requires 57.6 kJ mol⁻¹. Thus, exchange of one C–H proton and the O–H proton in CH₃OH^{•+} with the external water molecule can take place via a combination of the interconversion of **4b** and **5b** at a cost (relative to **4b**) of 9.5 kJ mol⁻¹, and rearrangements within **5b** (Figure 3c) at a cost (again relative to **4b**) of 20.1 kJ mol⁻¹. On the other hand, exchange of the other two carbon-bound protons requires interconversion of **4b** and **9b** via TS **10b** (accompanied by methyl group rotation in **9b**) at a considerably greater cost of 52.8 kJ mol⁻¹ (Figure 3b). Hence, our calculations predict that one of the original carbon-bound protons plus the oxygen-bound proton of CH₃OH^{•+} will exchange readily, while exchange of the remaining two carbon-bound protons will be considerably slower, consistent with experimental observations.

Complexation with water preferentially stabilizes the distonic ion [•]CH₂O⁺H₂ compared with the conventional ion CH₃OH^{•+}. Thus, the energy difference between **4b** and **5b** is 37.5 kJ mol⁻¹ and the energy difference between **9b** and **5b** is 34.5 kJ mol⁻¹ compared with an energy difference of 29.5 kJ mol⁻¹ between the isolated ions **1b** and **2b**.

c. The [CH₃NH₂/NH₃]^{•+} System. When CH₃NH₂^{•+} and NH₃ interact they are able to directly form the C–H···NH₃ bound complex **4c** (Figure 4a), which is analogous to **4a** and **4b**. As before, **4c** is able to rearrange in two ways, namely via the five-membered cyclic TS **7c** at a cost of just 3.4 kJ mol⁻¹ or via the three-membered cyclic TS **6c** at a cost of 3.6 kJ mol⁻¹ (Figure 4b). Again, the lower energy pathway (via TS **7c**) results in the exchange of internal and external protons, whereas the former (via TS **6c**) does not. At the MP2/6-31G(d,p) level, minima are found corresponding to both a [•]CH₂N⁺H₃···NH₃ complex (**5c₁**) and a [•]CH₂NH₂···N⁺H₄ complex (**5c₂**),¹⁸ separated by TS **12c**. However, at the G2** level, **12c** drops below **5c₁** in energy, suggesting that **5c₁** is likely to be transformed to **5c₂** with little or no barrier. The lowest energy dissociation of the [CH₃NH₂/NH₃]^{•+} system yields [•]CH₂NH₂ + NH₄⁺ at a cost of 78.5 kJ mol⁻¹ relative to **4c**. Thus, the interaction of NH₃ with CH₃NH₂^{•+} does not result in isomerization of CH₃NH₂^{•+} to the distonic ion [•]CH₂N⁺H₃ as the lowest energy process. Instead, intermolecular proton transfer from CH₃NH₂^{•+} to the base NH₃ is now energetically preferred to intramolecular proton migration from carbon to nitrogen within CH₃NH₂^{•+}.

The C–H···NH₃ bound complex **4c** may alternatively rearrange via TS **10c** to the N–H···NH₃ complex **9c** at a cost of 50.6 kJ mol⁻¹ (Figure 4c), analogous to the rearrangement observed for **4b** (see Figure 3b). In a similar manner to the [CH₃OH/H₂O]^{•+} system, the complex **9c** is found to be only marginally lower in energy than **4c** (by 2.3 kJ mol⁻¹). This complex (**9c**) may also be formed directly from the interaction of CH₃NH₂^{•+} and NH₃.

d. Comparisons. It is clear that the [CH₃F/HF]^{•+}, [CH₃OH/H₂O]^{•+}, and [CH₃NH₂/NH₃]^{•+} systems exhibit broadly similar features. In each case, the interaction of the base with the conventional ion leads to the formation of a C–H···base

(18) At the MP2/6-31G(d,p) level, **5c₂** is not the lowest energy conformation of the complex formed by the interaction of [•]CH₂NH₂ + NH₄⁺. However, it is the lowest energy form at the G2** level of theory.

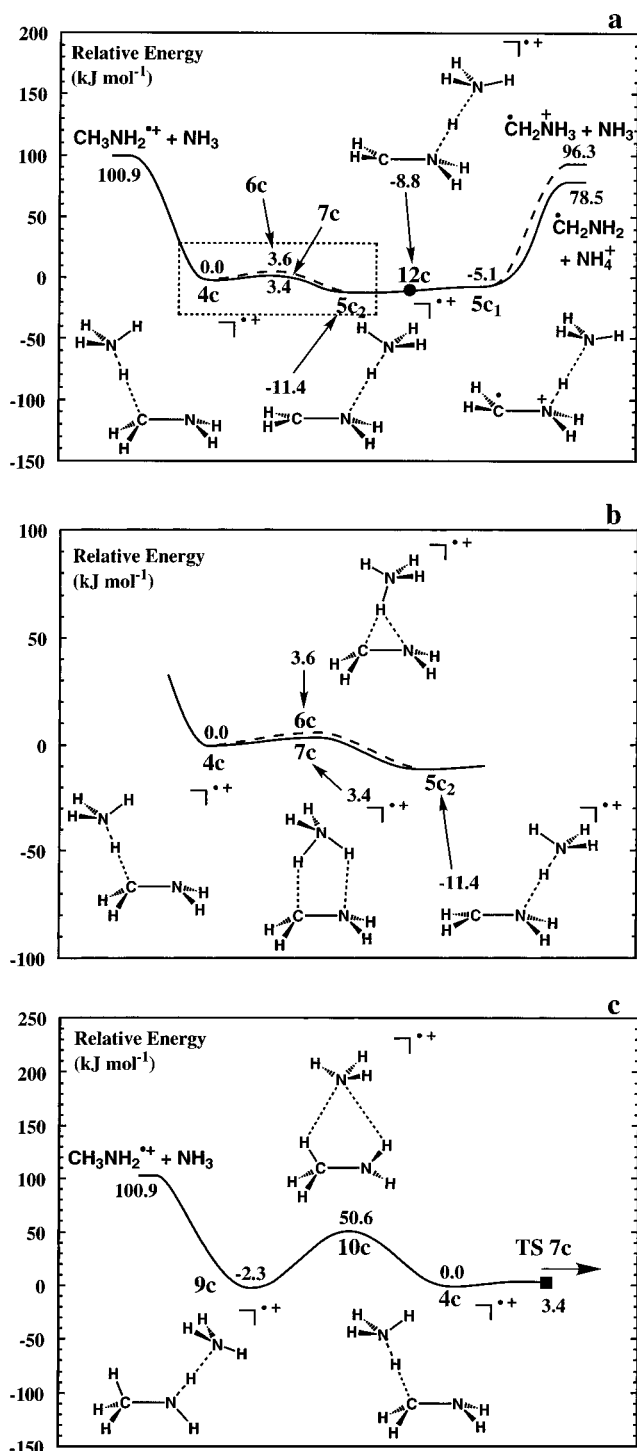


Figure 4. (a) Schematic energy profile for the ammonia-catalyzed interconversion of the methylamine and methyleneammonium radical cations involving the C-H...NH₃ (4c), N-H...NH₃ (5c₁), and •CH₂-NH₂...NH₄⁺ (5c₂) complexes. (b) Insert from part a showing in more detail the rearrangement of the C-H...NH₃ (4c) complex to the •CH₂-NH₂...NH₄⁺ complex (5c₂). (c) Schematic energy profile for interconversion of the C-H (4c) and N-H (9c) ammoniated forms of the methylamine radical cation (G2** at 0 K).

complex (4), which is then able to rearrange via pathways involving either a three-membered cyclic TS 6 or a five-membered cyclic TS 7. Interestingly, the transition structures 6 and 7 lie within 2.5 kJ mol^{-1} of one another in all three systems, despite their quite different structures. For the fluorine system, 6 lies slightly lower in energy whereas in the oxygen and nitrogen systems 7 lies slightly lower.

Table 1. Calculated^a G2** Proton Affinities of the Neutral Bases HF, H₂O, and NH₃, and the Carbon and Heteroatom Sites of the Associated Radicals (kJ mol^{-1})

| species ^b | proton affinity | species ^b | proton affinity |
|--------------------------|-----------------|--------------------------------------|-----------------|
| HF | 480.3 | CH₃O [•] | 696.9 |
| •CH₂F | 520.9 | •CH₂NH₂ | 825.5 |
| •CH₂F | 529.3 | •CH₂NH₂ | 830.1 |
| •CH₂OH | 660.6 | NH ₃ | 847.9 |
| H ₂ O | 682.3 | CH ₃ N [•] H | 850.0 |
| •CH₂OH | 690.1 | | |

^a Calculated at the G2** level at 0 K. ^b Site of protonation is in bold type.

The barrier to rearrangement starting from the C-H...base complex 4 decreases as one proceeds from the [CH₃F/HF]⁺ system (35.0 kJ mol^{-1}) to the [CH₃OH/H₂O]⁺ (9.5 kJ mol^{-1}) and [CH₃NH₂/NH₃]⁺ (3.4 kJ mol^{-1}) systems. This trend can be rationalized by considering the proton affinities of HF, H₂O, and NH₃ relative to the proton affinities at the carbon and heteroatom sites of •CH₂F, •CH₂OH, and •CH₂NH₂. Indeed, the proton-transfer catalysis mechanism can be thought of as base-assisted interconversion of the carbon (conventional ions) and heteroatom (dystonic ions) protonated forms of the parent radicals (CH₂X (X = F, OH, and NH₂)). Calculated G2** proton affinities for HF, H₂O, NH₃, and the associated radicals are presented in Table 1. We note that proton affinities calculated at similarly high levels have been shown to be in good agreement with experiment.¹⁹

In the [CH₃F/HF]⁺ system, the proton affinity of HF is lower than the proton affinities at both C and F in •CH₂F by about 40 and 50 kJ mol^{-1} , respectively (Table 1). The barrier for rearrangement of the C-H...FH bound complex 4a to the dystonic complex 5a is substantially reduced from its value of 102.0 kJ mol^{-1} for isolated CH₃F⁺ but is still significant at 35.0 kJ mol^{-1} (Figure 2a). In the [CH₃OH/H₂O]⁺ system, the proton affinity of H₂O is higher than that at C but lower than that at the O of •CH₂OH. In this case, H₂O is better able to draw a proton away from the carbon, enabling it to migrate to the oxygen site of •CH₂OH for the relatively low cost of 9.5 kJ mol^{-1} (Figure 3a). Finally, for the [CH₃NH₂/NH₃]⁺ system, the proton affinity of NH₃ is higher than that at either C or N in •CH₂NH₂ by about 22 and 18 kJ mol^{-1} , respectively. A very small barrier of 3.4 kJ mol^{-1} for the lower energy rearrangement of the C-H...NH₃ bound complex 4c is observed (Figure 4a). However, in this case intermolecular proton transfer leading to the formation of •CH₂NH₂ + NH₄⁺ is energetically preferred to intramolecular proton migration that would lead to •CH₂N⁺H₃ + NH₃.

Similar conclusions have been reached previously by Bohme.⁴ Such considerations may also help to rationalize the results of a recent experimental study²⁰ in which it was concluded that •CH₂P⁺H₃ did not interconvert with its conventional isomer CH₃PH₂⁺ when allowed to interact with a variety of neutral reagents. It would appear that the proton affinities of the reagents used were not in the range that would be expected to promote effective interconversion.

C. The Effects of Varying Base on the Isomerization of CH₃OH⁺ to •CH₂O⁺H₂. It is of interest now to compare the effects of interaction of a sequence of different bases (HF, H₂O, and NH₃) on the barrier and mechanism for a single isomerization, namely the rearrangement of CH₃OH⁺ to its dystonic isomer •CH₂O⁺H₂.

(19) See, for example: Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885.

(20) Schweighofer, A.; Chou, P. K.; Thoen, K. K.; Nanayakkara, V. K.; Keck, K.; Kuchen, W.; Kenttamaa, H. I. *J. Am. Chem. Soc.* **1996**, *118*, 11893.

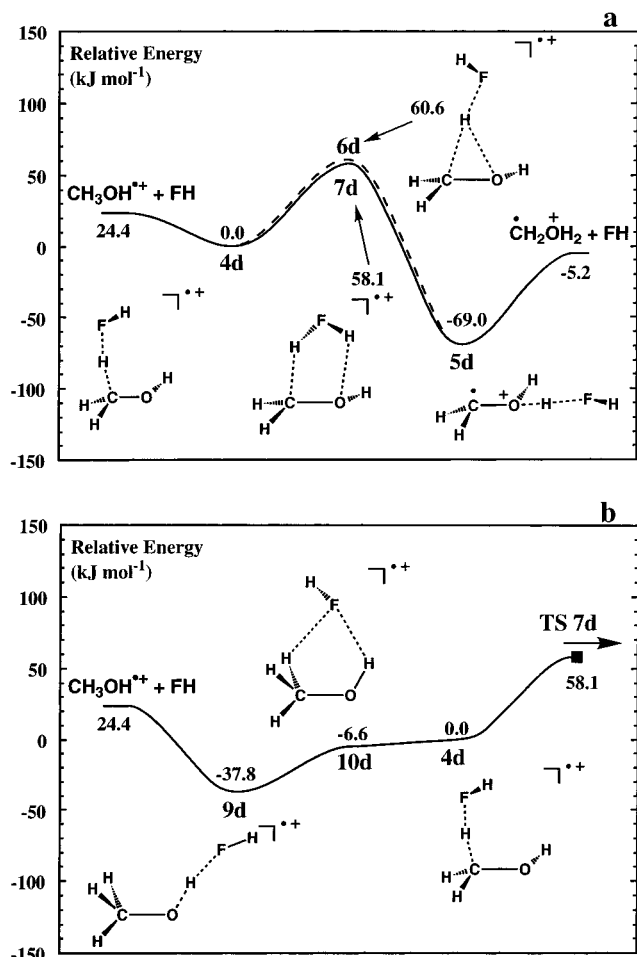


Figure 5. (a) Schematic energy profile for interconversion of the hydrogen fluoride complexes with methanol and methyleneoxonium radical cations involving the C–H···FH (**4d**) and O–H···FH (**5d**) bound complexes. (b) Schematic energy profile for interconversion of the C–H···FH (**4d**) and O–H···FH (**9d**) bound forms of the complex of methanol radical cation with hydrogen fluoride (G2** at 0 K).

a. [CH₃OH/HF]^{•+}. Interaction of HF with CH₃OH^{•+} can lead directly to the C–H···FH bound complex **4d** which, as in the previous cases, can rearrange in two ways to the distonic complex **5d**, lying 69.0 kJ mol⁻¹ lower in energy than **4d** (Figure 5a). The higher energy pathway proceeds via the three-membered cyclic TS **6d** at a cost of 60.6 kJ mol⁻¹, while the lower energy pathway proceeds via the five-membered cyclic TS **7d** at a cost of 58.1 kJ mol⁻¹. A complicating factor is that **4d** may alternatively rearrange via TS **10d** to form **9d**, in which HF is bound to CH₃OH^{•+} via the hydroxyl hydrogen (Figure 5b). At the MP2/6-31G(d,p) level, **4d** is located at a minimum on the potential surface, but at the G2** level, **10d** drops below **4d** in energy, suggesting that rearrangement to **9d** is likely to proceed with little or no barrier. It is thus not clear whether **4d** lies in a significant potential well.

From Figure 5 we can see that it requires 24.4 kJ mol⁻¹ for **4d** to dissociate to separated CH₃OH^{•+} + HF, significantly less energy than is required for it to isomerize to **5d** via TS **7d** (58.1 kJ mol⁻¹). Thus, the barrier to isomerization, while lower than that for isolated CH₃OH^{•+}, is greater than the energy required for dissociation to CH₃OH^{•+} + HF. Hence, HF is not an effective catalyst for the isomerization of CH₃OH^{•+} to [•]CH₂O⁺H₂.

b. [CH₃OH/NH₃]^{•+}. When NH₃ interacts with CH₃OH^{•+}, we find that intermolecular proton transfer from a C–H bond of CH₃OH^{•+} to NH₃ can take place followed by 1,2-hydrogen migration (Figure 6a). This could either be regarded as an NH₃-

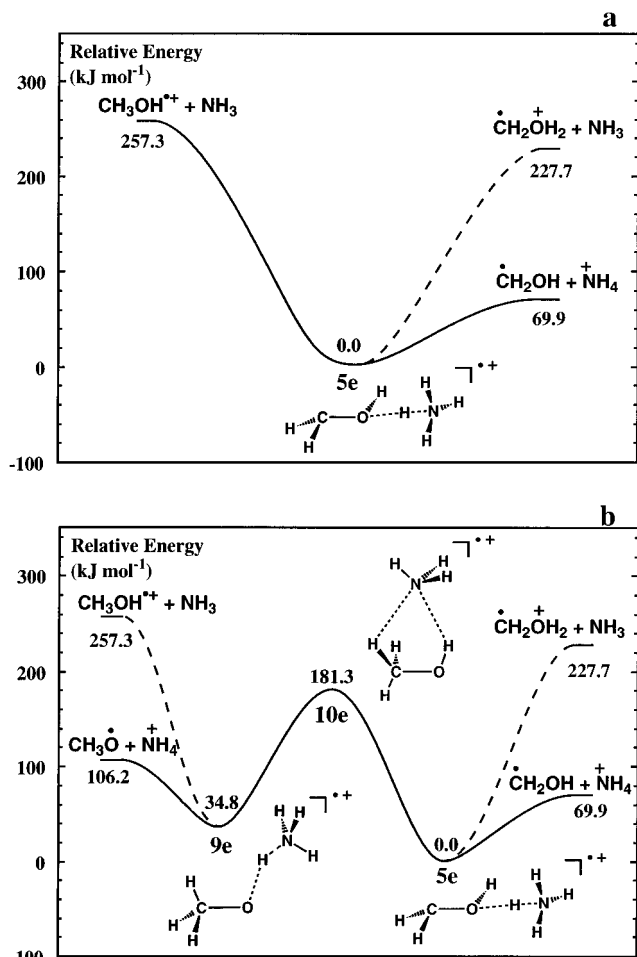


Figure 6. (a) Schematic energy profile for the interaction of the methanol radical cation and ammonia producing the distonic complex (**5e**). (b) Schematic energy profile for the interconversion of the ammoniated conventional ion (**9e**) and the ammoniated distonic ion (**5e**) (G2** at 0 K).

assisted 1,2-hydrogen migration or as a 1,2-NH₄⁺ migration. The product formed (**5e**) resembles a complex between [•]CH₂OH and NH₄⁺ (see Table S2 of the Supporting Information) rather than a complex of [•]CH₂O⁺H₂ with NH₃. The lowest energy dissociation of **5e** gives separated [•]CH₂OH + NH₄⁺ at a cost of 69.9 kJ mol⁻¹.

Alternatively, interaction of NH₃ with CH₃OH^{•+} may lead to **9e** (Figure 6b), which differs from the conventional ion–base complexes **9b–d** in that **9e** resembles a complex of CH₃O[•] with NH₄⁺ rather than a complex of CH₃OH^{•+} with NH₃ (Table S2). This arises because the proton affinity of NH₃ is significantly greater than that of CH₂O[•] (see Table 1). The lowest energy dissociation of **9e** gives separated CH₃O[•] + NH₄⁺ at a cost of 71.4 kJ mol⁻¹. In addition, **9e** may rearrange to **5e** at a cost of 146.5 kJ mol⁻¹ via TS **10e** (Figure 6b). Although TS **10e** is analogous to TS **10b–d**, the rearrangement reaction in this case differs because the structure corresponding to a C–H···NH₃ complex (notionally **4e**) collapses to **5e**. Thus **10e** connects **9e** and **5e** rather than **9e** and **4e**. As well as requiring considerably more energy than for dissociation to CH₃O[•] + NH₄⁺, this rearrangement process is substantially more energetically demanding than the rearrangements of **9b–d** via TS **10b–d**. This is due to the fact that for **9e** to rearrange to **5e** via TS **10e**, it is necessary first to effectively transfer a proton from NH₄⁺ to CH₃O[•], an energetically highly unfavorable process (Table 1). On the other hand, for **9b–d** the differences between the proton affinities of the bases and the heteroatom sites of

the parent radicals are smaller and generally favor the heteroatom. Thus, an energetically unfavorable proton transfer is not required.

c. Comparisons. Combining the results for the $[\text{CH}_3\text{OH}/\text{HF}]^+$, $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^+$, and $[\text{CH}_3\text{OH}/\text{NH}_3]^+$ systems allows us to comment on how interaction with a sequence of bases affects the rearrangement of CH_3OH^+ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$. The key parameters are the proton affinities of HF, H_2O , and NH_3 compared with those at C and O in $\cdot\text{CH}_2\text{OH}$ (Table 1). The proton affinity of HF ($480.3 \text{ kJ mol}^{-1}$) is substantially lower than the proton affinity at either C ($660.6 \text{ kJ mol}^{-1}$) or O ($690.1 \text{ kJ mol}^{-1}$) in $\cdot\text{CH}_2\text{OH}$, the proton affinity of H_2O ($682.3 \text{ kJ mol}^{-1}$) lies between the proton affinities at C and O, while NH_3 has a proton affinity ($847.9 \text{ kJ mol}^{-1}$) substantially higher than that at C or O of $\cdot\text{CH}_2\text{OH}$. Thus, the $[\text{CH}_3\text{OH}/\text{HF}]^+$, $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^+$, and $[\text{CH}_3\text{OH}/\text{NH}_3]^+$ systems represent a very useful spectrum of proton affinities and are representative of the three possible cases that might generally be encountered.

In the $[\text{CH}_3\text{OH}/\text{HF}]^+$ system, the barrier for rearrangement of CH_3OH^+ to its distonic isomer $\cdot\text{CH}_2\text{O}^+\text{H}_2$ is considerably less than in the isolated system but remains positive with respect to the separated reactants $\text{CH}_3\text{OH}^+ + \text{HF}$. This is a consequence of the low proton affinity of HF and shows that if the proton affinity of the interacting base is very low compared with those at C and X of $\cdot\text{CH}_2\text{X}$, effective proton-transfer catalysis will not occur. In addition, comparison of the $[\text{CH}_3\text{OH}/\text{HF}]^+$ system with the $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^+$ and $[\text{CH}_3\text{NH}_2/\text{NH}_3]^+$ systems clearly shows that the C–H \cdots base bound complex becomes less stable with respect to isomerization to the appropriate O–H \cdots base bound complex. Indeed, in the $[\text{CH}_3\text{OH}/\text{HF}]^+$ system the C–H \cdots base bound complex **4d** rearranges without a barrier to the O–H \cdots base bound complex **9d**.

In the $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^+$ system, the barrier to rearrangement becomes negative. As noted above, H_2O is ideally placed to catalyze the rearrangement because the proton affinity of H_2O lies between the proton affinities at C and O of $\cdot\text{CH}_2\text{X}$.

In the $[\text{CH}_3\text{OH}/\text{NH}_3]^+$ system, the barrier to rearrangement is again negative with respect to the reactants $\text{CH}_3\text{OH}^+ + \text{NH}_3$. However, in this case the products of the reaction are $\cdot\text{CH}_2\text{OH} + \text{NH}_4^+$ rather than $\cdot\text{CH}_2\text{O}^+\text{H}_2 + \text{NH}_3$. Thus, the use of a base whose proton affinity is greater than the proton affinity at C or X of the parent radical $\cdot\text{CH}_2\text{X}$ results in intermolecular proton transfer occurring rather than the desired intramolecular proton migration. In addition, in the case of very strong bases we no longer get formation of the C–H \cdots base bound complex, such a complex no longer being stable with respect to rearrangement to the $\cdot\text{CH}_2\text{OH}\cdots\text{NH}_4^+$ product ion.

D. The Effects of Varying Distonic and Conventional Radical Cations in Their Interaction with H_2O . We now examine the interaction of a sequence of conventional ions (CH_3F^+ , CH_3OH^+ , and CH_3NH_2^+) with the base H_2O .

a. $[\text{CH}_3\text{F}/\text{H}_2\text{O}]^+$. When H_2O and CH_3F^+ interact, intermolecular proton transfer from CH_3F^+ to H_2O , followed by proton migration to form **5f** can take place (Figure 7). This can either be regarded as an H_2O -assisted 1,2-hydrogen migration or a 1,2- H_3O^+ migration. The structure of **5f** resembles a complex between the protonated base (H_3O^+) and the parent radical ($\cdot\text{CH}_2\text{F}$) in a manner similar to **5e**. The lowest energy dissociation of **5f** gives separated $\cdot\text{CH}_2\text{F} + \text{H}_3\text{O}^+$ at a cost of 74.3 kJ mol^{-1} . Dissociation to the distonic ion $\cdot\text{CH}_2\text{O}^+\text{H}_2 + \text{H}_2\text{O}$ is a considerably higher energy process requiring $227.4 \text{ kJ mol}^{-1}$. Thus, H_2O does not effectively catalyze the isomerization of CH_3F^+ to its distonic isomer $\cdot\text{CH}_2\text{F}^+\text{H}$.

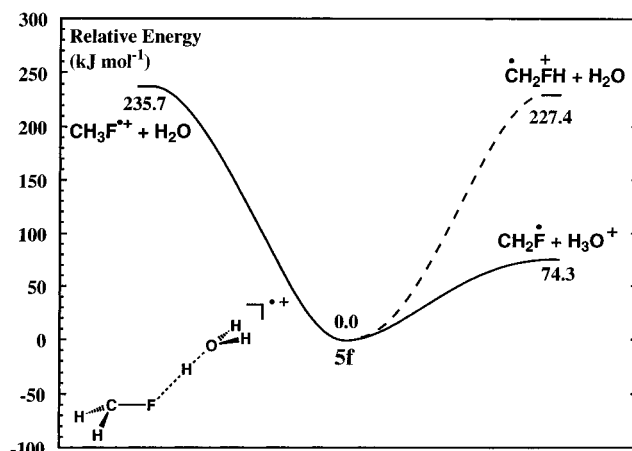


Figure 7. Schematic energy profile for the interaction of the methyl fluoride radical cation and water (G2^{**} at 0 K).

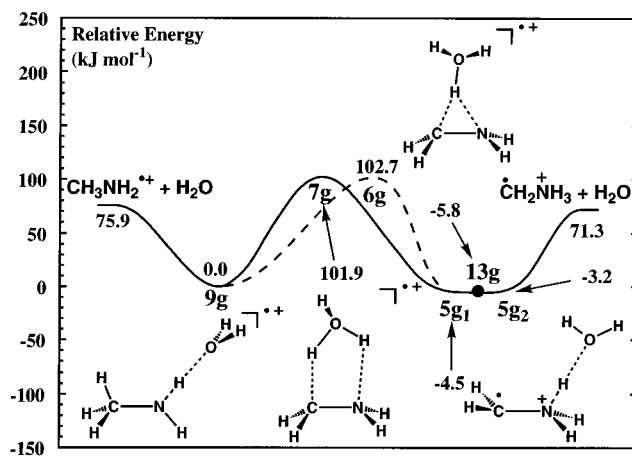


Figure 8. Schematic energy profile for the interconversion of the hydrated methylamine (**9g**) and methyleneammonium (**5g₁** and **5g₂**) radical cations (G2^{**} at 0 K).

b. $[\text{CH}_3\text{NH}_2/\text{H}_2\text{O}]^+$. When H_2O interacts with CH_3NH_2^+ , a C–H \cdots base bound complex is not formed but instead the hydrated methylamine radical cation **9g**, which is analogous to **9b–d**, is formed (Figure 8). There are then two ways by which **9g** may rearrange to the distonic complex **5g₁**. The higher energy pathway proceeds via the three-membered cyclic TS **6g** at a cost of $102.7 \text{ kJ mol}^{-1}$, while the lower energy pathway proceeds via the five-membered cyclic TS **7g** at a cost of $101.9 \text{ kJ mol}^{-1}$. We have characterized two isomers of the distonic complex, **5g₁** and **5g₂**, differing as to the point of attachment of the water molecule to an N–H bond, with energies relative to **9g** of -4.5 and -3.2 kJ mol^{-1} , respectively. The slightly lower energy form is **5g₁** (illustrated in Figure 8), while in **5g₂** the water is bonded in a gauche-type conformation (see Table S2 of the Supporting Information for details). At the G2^{**} level, TS **13g** drops below the energy of both **5g₁** and **5g₂**, suggesting that there is little or no barrier separating these species.

It requires 75.9 kJ mol^{-1} for **9g** to dissociate to separated $\text{CH}_3\text{NH}_2^+ + \text{H}_2\text{O}$, which is less than the energy required for it to rearrange to **5g₁** via TS **7g**. Thus, the barrier to isomerization, while lower than that for isolated CH_3NH_2^+ , remains positive relative to separated $\text{CH}_3\text{NH}_2^+ + \text{H}_2\text{O}$. Hence, H_2O is not a particularly effective catalyst for the isomerization of CH_3NH_2^+ to $\cdot\text{CH}_2\text{N}^+\text{H}_3$.

c. Comparisons. The results for the $[\text{CH}_3\text{F}/\text{H}_2\text{O}]^+$, $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^+$, and $[\text{CH}_3\text{NH}_2/\text{H}_2\text{O}]^+$ systems can again be readily rationalized by comparing the proton affinities of the base H_2O with the proton affinities at C and at F, O, and N of the parent

radicals $\cdot\text{CH}_2\text{F}$, $\cdot\text{CH}_2\text{OH}$, and $\cdot\text{CH}_2\text{NH}_2$. The proton affinity of H_2O is substantially greater than the proton affinity at C or F of $\cdot\text{CH}_2\text{F}$ so that in the $[\text{CH}_3\text{F}/\text{H}_2\text{O}]^{+\bullet}$ system, despite a negative barrier for proton migration, intermolecular proton transfer to give $\cdot\text{CH}_2\text{F} + \text{H}_3\text{O}^+$ rather than intramolecular proton migration to give $\cdot\text{CH}_2\text{F}^+\text{H} + \text{H}_2\text{O}$ takes place. So water is not an effective catalyst for the transformation of $\text{CH}_3\text{F}^{+\bullet}$ to $\cdot\text{CH}_2\text{F}^+\text{H}$. As we have already noted, the proton affinity of H_2O lies between the proton affinities of $\cdot\text{CH}_2\text{OH}$ at C and O so water is a very effective catalyst for the rearrangement of $\text{CH}_3\text{OH}^{+\bullet}$ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$. Finally, in the $[\text{CH}_3\text{NH}_2/\text{H}_2\text{O}]^{+\bullet}$ system, the barrier to isomerization, although less than for isolated $\text{CH}_3\text{NH}_2^{+\bullet}$, is positive relative to separated $\text{CH}_3\text{NH}_2^{+\bullet} + \text{H}_2\text{O}$. This is a result of H_2O having a proton affinity considerably less than that at either C or N of $\cdot\text{CH}_2\text{NH}_2$. Thus, H_2O is not a particularly effective catalyst for the interconversion of $\text{CH}_3\text{NH}_2^{+\bullet}$ and its distonic isomer $\cdot\text{CH}_2\text{N}^+\text{H}_3$.

E. The Spectator Mechanism. An alternative mechanism for interconversion of $\text{CH}_3\text{OH}^{+\bullet}$ and $\cdot\text{CH}_2\text{O}^+\text{H}_2$, in which H_2O remains bound to the hydroxyl hydrogen throughout the isomerization process, was also investigated. We refer to this as the "spectator" mechanism because the water molecule is not directly involved in the hydrogen migration. In the case of the $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^{+\bullet}$ system, this mechanism corresponds to the direct isomerization of the hydrated methanol radical cation (**9b**) to the hydrated methyleneoxonium ion (**5b**) via TS **14b** (see Figure 9a). This mechanism has been studied previously at a lower level of theory,²¹ and we have also reported preliminary results from the present study.⁶ The rearrangement via TS **14b** requires $114.4 \text{ kJ mol}^{-1}$, which is slightly less than the energy of separated $\text{CH}_3\text{OH}^{+\bullet} + \text{H}_2\text{O}$. However, the energy difference is sufficiently small that, combined with the unfavorable entropy associated with this rearrangement compared with dissociation, it is unlikely to be an effective pathway. In addition, the energy requirement is greater than that required for the lowest energy dissociation of **9b** to give $\cdot\text{CH}_2\text{O}^+\text{H}_2 + \text{H}_2\text{O}$, and it is also substantially greater than the barrier found for the proton-transfer catalysis mechanism for $[\text{CH}_3\text{OH}/\text{H}_2\text{O}]^{+\bullet}$ (see Figure 3).

Strikingly, the barrier for rearrangement via the spectator mechanism and TS **14b** is also slightly higher than the barrier for isomerization of isolated $\text{CH}_3\text{OH}^{+\bullet}$ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$ ($108.0 \text{ kJ mol}^{-1}$, Figure 1b). Thus, the complexation of H_2O to $\text{CH}_3\text{OH}^{+\bullet}$ via the hydroxyl hydrogen actually leads to an increase in the barrier for the direct isomerization of $\text{CH}_3\text{OH}^{+\bullet}$ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$.

We have also characterized analogous spectator mechanisms for the $[\text{CH}_3\text{OH}/\text{HF}]^{+\bullet}$ and $[\text{CH}_3\text{OH}/\text{NH}_3]^{+\bullet}$ systems (see Figure 9, parts b and c), in which the bases HF and NH_3 have replaced H_2O as the reaction spectators. The barrier heights for these three spectator mechanisms, as well as those for isomerization of isolated $\text{CH}_3\text{OH}^{+\bullet}$ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$ and for $\text{CH}_3\text{O}^\bullet$ to $\cdot\text{CH}_2\text{OH}$, are presented in Table 2. For bases of low proton affinity, the barrier height for the spectator mechanism is close to the barrier for isomerization of isolated $\text{CH}_3\text{OH}^{+\bullet}$ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$, as might have been expected. The pertinent observations are that (a) the barrier for conversion of $\text{CH}_3\text{O}^\bullet$ to $\cdot\text{CH}_2\text{OH}$ is greater than the barrier for conversion of $\text{CH}_3\text{OH}^{+\bullet}$ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$ and (b) as the proton affinity of the base increases, the barrier height increases, approaching that for interconversion of the isomeric radicals $\text{CH}_3\text{O}^\bullet$ and $\cdot\text{CH}_2\text{OH}$.

These observations may be readily rationalized by considering the proton affinities of HF, H_2O , NH_3 , and $\text{CH}_3\text{O}^\bullet$ (see Table 1), and keeping in mind that the base remains bound to the hydroxyl hydrogen throughout the isomerization process. The proton affinity of HF is considerably lower than that of $\text{CH}_3\text{O}^\bullet$.

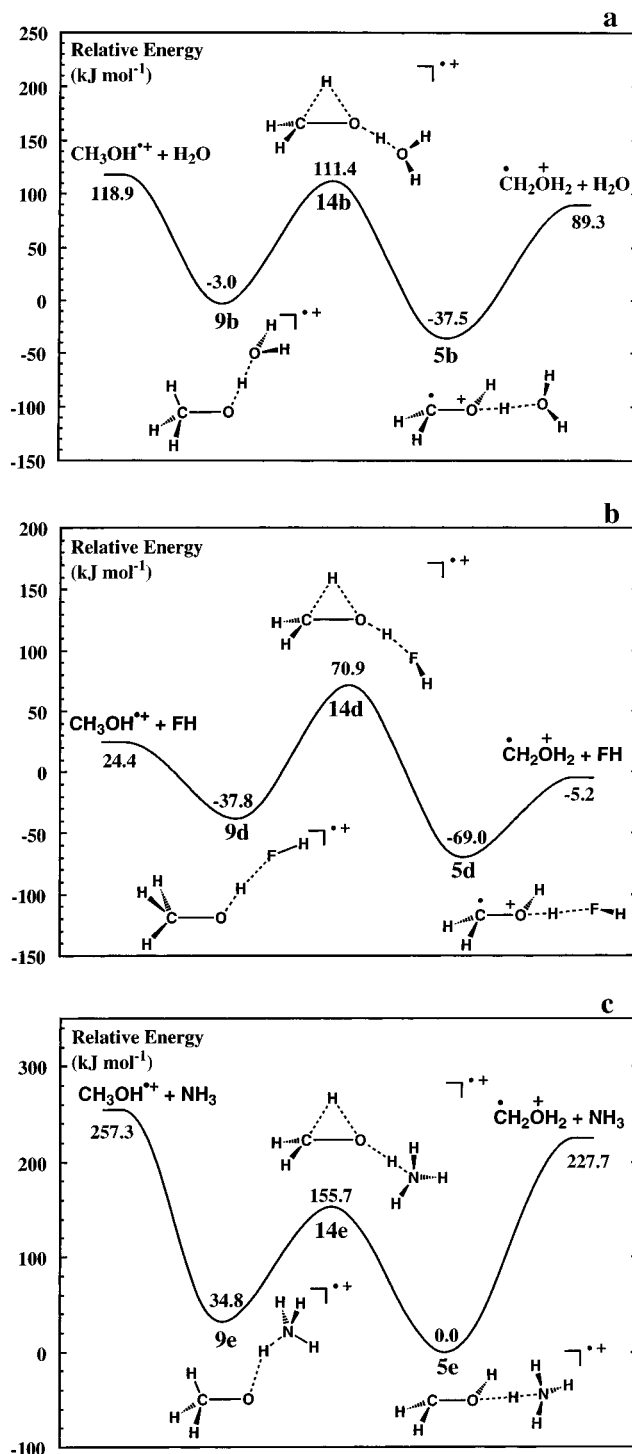


Figure 9. Schematic energy profiles for rearrangements involving a "spectator" O-H-bound water molecule: (a) interconversion of the hydrated methanol (**9b**) and methyleneoxonium (**5b**) radical cations, (b) interconversion of HF complexes of the methanol (**9d**) and methyleneoxonium (**5d**) radical cations, and (c) interconversion of NH_3 complexes of the methanol (**9e**) and methyleneoxonium (**5e**) radical cations ($G2^{**}$ at 0 K).

As a result, the $\text{CH}_3\text{OH}^{+\bullet}$ moiety in the $\text{CH}_3\text{O}-\text{H}\cdots\text{base}^{+\bullet}$ complex formed by the interaction of HF and $\text{CH}_3\text{OH}^{+\bullet}$ is still essentially intact, as indicated by only a minor lengthening of the $\text{CH}_3\text{O}-\text{H}$ bond (see Table 2). The rearrangement process is essentially that of $\text{CH}_3\text{OH}^{+\bullet}$ itself. Replacement of HF by increasingly strong bases results in the ion-base complex increasingly resembling a complex between $\text{CH}_3\text{O}^\bullet$ and the protonated base so that, in the case of NH_3 , which has a proton affinity significantly greater than that of $\text{CH}_3\text{O}^\bullet$, intermolecular

(21) Burcl, R.; Hobza, P. *Theor. Chim. Acta* **1993**, *87*, 97.

Table 2. Calculated^a Barrier Heights and O–H Bond Lengths (Å) for the Spectator Mechanism for the Rearrangement of CH_3OH^+ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$ and Related Reactions (kJ mol^{-1})

| | base | barrier height ^a (kJ mol^{-1}) | O–H bond length ^b (Å) |
|--|------------------|---|-------------------------------------|
| $\text{CH}_3\text{OH}^+ \rightarrow \text{CH}_2\text{O}^+\text{H}_2$ | | 108.0 | 0.990 |
| | HF | 108.7 | 1.029 |
| | H ₂ O | 114.4 | 1.209 |
| | NH ₃ | 120.9 | 1.701 |
| $\text{CH}_3\text{O}\cdot \rightarrow \cdot\text{CH}_2\text{OH}$ | | 127.6 | |

^a Calculated at the G2** level at 0 K. ^b Length of the O–H bond (Å) in isolated $\text{CH}_3\text{O–H}^+$ and in the $[\text{CH}_3\text{O–H}\cdots\text{base}]^+$ complexes.

proton transfer from CH_3OH^+ to the base is very advanced. This is also reflected in the calculated lengthening of the O–H bond (see Table 2). So now the rearrangement process corresponds effectively to rearrangement within $\text{CH}_3\text{O}\cdot$. Thus, as increasingly strong bases are used, the spectator mechanism changes from resembling the rearrangement of CH_3OH^+ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$ to a mechanism resembling the interconversion of the radicals $\text{CH}_3\text{O}\cdot$ and $\cdot\text{CH}_2\text{OH}$. Because the barrier for the isomerization of $\text{CH}_3\text{O}\cdot$ to $\cdot\text{CH}_2\text{OH}$ is greater than for the isomerization of CH_3OH^+ to $\cdot\text{CH}_2\text{O}^+\text{H}_2$, the barrier for the spectator mechanism increases as the strength of the interacting base increases.

Analogous “spectator” mechanisms were also found in the $[\text{CH}_3\text{NH}_2/\text{NH}_3]^+$ and $[\text{CH}_3\text{NH}_2/\text{H}_2\text{O}]^+$ systems (see Figures S1 and S2 of the Supporting Information), with the trends observed being similar to those discussed above.

Concluding Remarks

The rearrangements of the isolated conventional ions CH_3X^+ ($\text{X} = \text{F}, \text{OH}, \text{and NH}_2$) to their distonic isomers $\cdot\text{CH}_2\text{X}^+\text{H}$ are calculated to be impeded by large barriers of 102.0, 108.0, and 155.8 kJ mol^{-1} , respectively. Because the lowest energy dissociations of the conventional ions require much less energy, the conventional ions will dissociate in preference to rearranging to their distonic isomers.

When the neutral bases HF, H₂O, and NH₃ are allowed to interact with the above conventional ions, CH_3X^+ , a lowering of the barrier to isomerization is observed for all the resulting ion–base systems. However, the extent of the lowering of the barrier, hence the success of the base in catalyzing the isomerization of the conventional ions to their distonic isomers, is found to depend on the proton affinities of the base relative to the proton affinities at C and X in the parent radicals $\cdot\text{CH}_2\text{X}$.

If the proton affinity of the base is considerably lower than the proton affinities at C and X of $\cdot\text{CH}_2\text{X}$, the barrier to isomerization remains positive relative to separated base plus CH_3X^+ and greater than the energy required for the lowest

energy dissociation of the ion–base system. Thus, isomerization of the conventional ion to its distonic isomer will not be a favorable process.

If the proton affinity of the base lies between the proton affinities at C and X of the parent radical, the barrier to isomerization becomes negative relative to the separated reactants ($\text{CH}_3\text{X}^+ + \text{base}$). In addition, the barrier is found to be lower than the energy required for the lowest energy dissociation of the ion–base system. Thus, interaction of the base with the conventional ion successfully allows interconversion with the distonic isomer by the mechanism of proton-transport catalysis in these cases. In fact, proton-transport catalysis is predicted to occur even when the proton affinity of the base is lower than the lower proton affinity site of $\cdot\text{CH}_2\text{X}$, provided that the difference in proton affinities is not too great.

If the proton affinity of the base is greater than that at both C and X of $\cdot\text{CH}_2\text{X}$, the barrier to proton migration is lowered even further. However, instead of intramolecular proton migration, intermolecular proton transfer from the ion to the base is observed. Hence, successful interconversion of the conventional and distonic ions does not occur.

An alternative mechanism for involving the base in the interconversion of CH_3OH^+ and $\cdot\text{CH}_2\text{O}^+\text{H}_2$ in the $[\text{CH}_3\text{OH}/\text{base}]^+$ systems was also examined. In this so-called “spectator” mechanism, the base remains bound to the hydroxyl proton throughout the isomerization process. As the proton affinity of the base is increased, the $[\text{CH}_3\text{O–H}\cdots\text{base}]^+$ and $[\text{CH}_2\text{OH–H}\cdots\text{base}]^+$ complexes increasingly resemble complexes between $\text{CH}_3\text{O}\cdot$ or $\cdot\text{CH}_2\text{OH}$ and the protonated base, respectively. As a consequence, the barriers for such spectator rearrangements are found to be greater than that for the isolated ions (CH_3OH^+ and $\cdot\text{CH}_2\text{O}^+\text{H}_2$), approaching that for interconversion of the isomeric radicals $\text{CH}_3\text{O}\cdot$ and $\cdot\text{CH}_2\text{OH}$ as the proton affinity of the base is increased.

Acknowledgment. We thank Professors Henri Audier, Steen Hammerum, and Terry McMahon for helpful discussions and gratefully acknowledge generous allocations of time on the VP-2200 and VPP-300 supercomputers and the SGI-Power Challenge of the Australian National University Supercomputer Facility.

Supporting Information Available: Total G2** energies, with and without the inclusion of MP2/6-31G(d,p) zero-point vibrational energies (Table S1), archive entries for the MP2/6-31G(d,p) optimized geometries (Table S2), and schematic representations of the “spectator” mechanism for the $[\text{CH}_3\text{NH}_2/\text{NH}_3]^+$ (Figure S1) and $[\text{CH}_3\text{NH}_2/\text{H}_2\text{O}]^+$ (Figure S2) systems (21 pages). See any current masthead page for ordering and Internet access instructions.

JA970785H