ELSEVIER

International Journal of Mass Spectrometry 222 (2003) 41–48

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

# The water-solvated methanol ion and its isomers: experiment and theory

Jie Cao, Ya-Ping Tu, Weixing Sun, John L. Holmes*

*Chemistry Department, University of Ottawa, 10 Marie-Curie St., P.O. Box 450, Stn. A., Ottawa, Ont., Canada K1N 6N5*

Received 8 March 2002; accepted 9 July 2002

This paper is dedicated to Jack Beauchamp on the occasion of his 60th birthday, wishing him continued success in his pursuit of the elusive chemistry of gas-phase ions.

## Abstract

Tandem mass spectrometry combined with ab initio calculations was used to explore the chemistry of the water-solvated methanol cation and its isomers, including the distonic methanol ion solvated by water, $^{\bullet}CH_2OH_2{}^+/H_2O$ (**I**), the methanol molecular ion associated with water, $CH_3OH^{\bullet+}/H_2O$ (**II**), and protonated methanol bound with a hydroxyl radical, $CH_3OH_2{}^+/HO^{\bullet}$ (**IV**). Another ion, $[H_2O\cdots H–CH_2OH^{\bullet+}]$ (**III**), where the water molecule is attached to a methyl H of the methanol cation, proved inaccessible experimentally although it was predicted to be stable in a shallow potential well by theoretical calculations. The ions were generated by collision-induced loss of a radical or atom from appropriate proton bound molecular pairs. The heats of formation of ions (**I**) to (**IV**) were calculated to be 448, 482, 486 and 538 kJ/mol, respectively. Ions (**I**), (**II**) and (**IV**) can be identified by their metastable ion and collision-induced dissociation mass spectra. A partial potential energy surface linking the isomers is used to discuss the experimental data obtained with deuterium-labeled species. (Int J Mass Spectrom 222 (2003) 41–48)

*Keywords:* Tandem mass spectrometry; Dissociation mass spectra; Metastable ion

## 1. Introduction

Many significant advances in our understanding of the gas phase chemistry of small organic ions have accrued over the past 30 years. Among these advances has been the development of experimental methods for the determination of ion structures and their energetics [1]. The number of stable isomers for simple organic cations far exceeds those of their neutral counterparts; e.g., there are only three neutral $C_2H_4O$ molecules, oxirane, acetaldehyde, and under appropriate conditions, vinyl alcohol. However, at least 11 $C_2H_4O^{\bullet+}$ isomers have been shown by ab initio calculations to be stable, 7 of which have been identified by experiments [2,3]. Apart from establishing their stability, in order to understand relationships between the ions more fully, it is important to know the energy barriers that separate such isomers.

In many instances the energy barrier separating two isomers, $A^{\bullet+}$ and $B^{\bullet+}$, exceeds that of the lowest energy dissociation channel of one of them, and therefore they cannot freely interconvert without decomposition.

---

* Corresponding author. E-mail: jholmes@science.uottawa.ca

1387-3806/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
*PII* S1387-3806(02)00949-1

High barriers leave the isomers in independent potential wells, between which there is no communication, i.e., stable $A^{\bullet+}$ cannot convert to stable $B^{\bullet+}$. In such a case their metastable ion (MI) mass spectra will be characteristic of only the more labile structure. Distinguishing between them will best be achieved by comparing their collision-induced dissociation (CID) mass spectra, which sample ions from the bottom of the wells to their dissociation or isomerization limit.

A good example of this behavior is that of the $CH_4O^{\bullet+}$ isomers, ionized methanol and its more stable distonic form, $^{\bullet}CH_2OH_2{}^{+}$, whose enthalpies of formation, $\Delta_f H^\circ$, differ by only 30 kJ/mol. The barrier for rearrangement of the distonic ion to the conventional isomer is large (137 kJ/mol) and this transition state lies 43 kJ/mol above the dissociation limit of $CH_3OH^{\bullet+}$ to $CH_2OH^{+} + H^{\bullet}$ [4]. Interconversion between these stable isolated ions is thus prevented. The excess energy in the dissociating distonic methanol ion makes the metastable peak for H loss broader than that for the methanol molecular ion. Their CID mass spectra are even more strikingly structure characteristic.

In recent years attention has been drawn to the ability of polar substrate molecules, when electrostatically bound to an ion, to bring about the isomerization at a much lower energy, which could be well below the dissociation limit. Substrate assistance in the isomerization has been termed "proton transport catalysis" [5], and many catalysts have been studied in both simple [6,7] and complex systems [8]. The key requirement [5] for this mechanism to work is that the proton affinity of the catalyst X should lie between those of the two sites (A and B) in the ions generated by proton transfer to X, i.e., for an even electron ion:

$$\frac{[\mathrm{H{-}A{-}B}]^{+}}{\mathrm{X}} \rightarrow \frac{[\mathrm{A{-}B}]^{+}}{\mathrm{HX}^{+}} \rightarrow \frac{[\mathrm{A{-}B{-}H}]^{+}}{\mathrm{X}}$$

and for an odd electron ion

$$\frac{[\mathrm{H{-}A{-}B}]^{\bullet+}}{\mathrm{X}} \rightarrow \frac{[\mathrm{A}^{\bullet}\mathrm{{-}B}]}{\mathrm{HX}^{+}} \rightarrow \frac{[\mathrm{A}^{\bullet}\mathrm{{-}B{-}H}^{+}]}{\mathrm{X}}$$

Note that the latter produces a distonic ion.

For the methanol ions, the first experimental study of their catalyzed interconversion [9] was performed by characterizing the *m*/*z* 32 ion generated in a chemical ionization ion source with 1:10 methanol/water mixture as the reagent gas. It was found that at the highest pressures attained, the residual *m*/*z* 32 ion had the distonic structure. This had presumably resulted from bimolecular interactions of ionized methanol with water. The reaction was first noticed in an explicit bimolecular encounter between the methanol ion and $H_2O$ in an FT-ICR study [10]. The potential energy surface for the catalysis in the $CH_3OH^{\bullet+}/H_2O$ system has been investigated in considerable detail by Audier and coworkers [11a], where three stable $CH_4O^{\bullet+}/H_2O$ configurations have been identified. These were the species $^{\bullet}CH_2O\underline{H}_2{}^{+}/H_2O$, the global minimum, $CH_3O\underline{H}^{\bullet+}/H_2O$ (**II**), and $H_2O/\underline{H}{-}CH_2OH^{\bullet+}$ (**III**), all $\underline{H}$-bridged ions. Their structures and relative energies will be described further later in the Section 4.

Water-assisted isomerization of the methanol ions may follow the proton-transport catalysis mechanism because the proton affinity of water lies exactly between that of the $^{\bullet}CH_2OH$ radical at C and O. However, it is found that isomerization of the methanol ions can also be catalyzed by noble gases [12] and methanol itself [13a]. The proton affinity of these molecules is either much lower or higher than that of the $^{\bullet}CH_2OH$ radical (at either C or O), indicating that the catalysis may involve a 1,2-H atom transfer mechanism.

In recent studies of solvated distonic ions we [13] have developed a strategy to generate and investigate the characteristics of stable and metastable distonic ion/molecule adducts, which show significant difference from the bimolecular encounters between the ion and the catalyst. The ion/molecule adducts were prepared by collision-induced loss of an appropriate radical from mass selected proton bound molecule pairs. For example, collision-induced loss of $CH_3{}^{\bullet}$ from $(CH_3CD_2OH)H^{+}(CD_3OH)$ yields $^{\bullet}CD_2OH_2{}^{+}/CD_3OH$, the distonic methanol ion–methanol pair.

In this work we report on the chemistry of ions (**I**), (**II**) and (**III**) and that of a new isomer, $CH_3OH_2{}^{+}/^{\bullet}OH$ (**IV**), carried out by tandem mass spectrometry together with high level theoretical calculations.

## 2. Experimental

All experiments were carried out on a modified ZAB 3F tandem mass spectrometer [14] with BEE geometry (VG Analytical, Manchester, UK). Metastable ion and collision-induced dissociation mass spectra were acquired with the ZABCAT program [15], by averaging sufficient consecutive scans, at an accelerating voltage of 8 kV. Helium was used as the target gas for the CID experiments at a cell pressure of 0.5–1 $\times 10^{-7}$ mbar, which for these ions causes ca. 15% attenuation of the mass selected ion beam. Proton bound pairs were generated by introducing the appropriate species through the septum inlet to the chemical ionization ion source, which was maintained at a temperature of 150 °C and a total pressure of ca. $1 \times 10^{-4}$ mbar. The proton bound pair was selected by the magnet and subjected to collisional activation in the second field-free region (FFR); the resulting $CH_4O^{\bullet+}/H_2O$ isomer or isotopomer was transmitted to the third FFR, where its MI and CID mass spectra were observed. The compounds were of research grade and deuterium-labeled molecules, of 99.9% isotope purity, were obtained from CDN isotopes (Montreal, Que., Canada).

Ion (**I**) was prepared in an earlier report [13a] by collision-induced loss of $H^\bullet$ from $CH_3OH_2^+/H_2O$

Table 1
MI and CID mass spectra of the water-solvated methanol ion, its isomers and isotopomers (all values are the average of repeat determinations)

| Source ion (*m/z*) | Neutral lost | Precursor ion (*m/z*) | Mode | Product ions (*m/z*) (%) |
|---|---|---|---|---|
| $CH_3OH_2^+/H_2O$ (51) | $H^\bullet$ | $^\bullet CH_2OH_2/H_2O$ (50) **I** | MI | 19 (~1)<br>32 (31)<br>49 (100) |
| | | | CID | 19 (17)<br>31 (19) 32 (100) 33 (40)<br>49 (68) |
| $CH_3OD_2^+/D_2O$ (55) | $H^\bullet$ | $^\bullet CH_2OD_2/D_2O$ (54) **I**-$d_4$ | MI | 22 (~1)<br>34 (78) 35 (100) 36 (21)<br>52 (6) 53 (41) |
| | | | CID | 20 (5) 21 (10) 22 (25)<br>33 (8) 34 (100) 35 (80) 36 (15)<br>52 (5) 53 (24) |
| $(CH_3)_2OH^+/H_2O$ (65) | $CH_3^\bullet$ | $CH_3OH^{\bullet+}/H_2O$ (50) **II** | MI | 32 (31)<br>49 (100) |
| | | | CID | 19 (17)<br>31 (20) 32 (100)<br>49 (70) |
| $(CH_3)_2OD^+/D_2O$ (68) | $CH_3^\bullet$ | $CH_3OD^{\bullet+}/D_2O$ (53) **II**-$d_3$ | MI | 33 (13) 34 (36) 35 (34)<br>51 (6) 52 (100) |
| | | | CID | 20 (10) 21 (20) 22 (10)<br>32 (12) 33 (43) 34 (100) 35 (45)<br>50 (11) 51 (20) 52 (68) |
| $(CH_3OH)_2H^+$ (65) | $CH_3^\bullet$ | $CH_3OH_2^+/HO^\bullet$ (50) **IV** | MI | 19 (10)<br>32 (100)<br>49 (6) |
| | | | CID | 19 (10)<br>32 (100) 33 (82)<br>49 (3) |
| $(CH_3OD)_2D^+$ (68) | $CH_3^\bullet$ | $CH_3OD_2^+/DO^\bullet$ (53) **IV**-$d_3$ | MI | 20 (3) 21 (10) 22 (3)<br>33 (72) 34 (100) 35 (22)<br>52 (10) |
| | | | CID | 20 (1) 21 (4) 22 (1)<br>32 (2) 33 (28) 34 (40) 35 (100)<br>52 (5) |

and $CH_3OD_2{}^+/D_2O$. In the present study it was also prepared by collision-induced loss of $CH_3{}^\bullet$ from $CH_3CH_2OH_2{}^+/H_2O$ and from $CH_3CH_2OD_2{}^+/D_2O$, and its behavior was the same as reported before. Preparation of the other ions is given in Table 1 (see Section 4). Note that ion **III**, $[H_2O\cdots H–CH_2OH^{\bullet+}]$, where the water molecule is attached to a methyl hydrogen, exists only in a shallow potential well [11], and as such could not be characterized by experiments.

The collisionally generated ion/molecule pairs produced in all these experiments were small signals in the CID mass spectra of their precursor, proton bound pairs, being typically 2–5% of the base peak. However, the signal-averaged third FFR mass spectra of these transmitted fragment ions were of good quality, similar to those shown in [13a].

## 3. Computational procedures

Standard ab initio molecular orbital calculations [16] were carried out using the GAUSSIAN 98 suite of programs [17]. The geometry of all species were optimized at B3-LYP/6-31+G(d) level of theory. Vibrational frequencies were also obtained at this level.

Energies for each B3-LYP/6-31+G(d) geometry were obtained at the G3 theory level. This approximates the energy of a species at the QCISD(T)/G3 large level of theory by a series of additive corrections to a base MP4/6-31+G(d) energy. The G3 large basis set is a modified version of the standard 6-311+G(3df,2p) basis set, in which more polarization functions are added to first-row elements (3d,2f), fewer to second-row elements (2df), and core polarization functions are also incorporated. Details of the properties of the G3 large basis set can be found in the original publication [18]. G3 includes a scaled (by 0.9614 [19]) B3-LYP/6-31+G(d) zero-point vibrational energy (ZPE), spin orbit corrections for atoms, and the use of the MP2(full)/G3 large calculation to take into account core-correlation contributions. Finally, an empirical higher-level correction (HLC) accounts for residual basis-set errors. The G3 total energies were converted to heats of formation using the atomization method of Nicolaides et al. [20]. Thermal corrections to 298 K used the scaled B3-LYP/6-31+G(d) frequencies and known thermal corrections for the elements. Ion binding energies were evaluated from the energy differences between each ion and those calculated for the appropriate dissociation products.

## 4. Results and discussion

The ions (**I**), (**II**) and (**IV**) were made as indicated in Table 1 which lists the MI and CID data for the various isotopically-labeled species. Data are grouped in rows for different reaction channels.

Water and hydrogen atom losses and the formation of protonated water are the three reactions observed under MI and/or CID conditions. Ions (**I**) and (**II**) are closely similar in their MI mass spectra; both show the loss of a hydrogen atom as the major dissociation channel, a process that is minor with ion (**IV**). $H^\bullet$ loss for (**I**) is not collision sensitive, indicating that a high energy rearrangement precedes this reaction. All three ions display loss of water in the metastable ion time frame with varied degrees of H/D mixing when they are partially deuterium labeled. For ion (**I**), a complete scrambling of all H/D atoms is observed; considerable but incomplete H/D randomization occurs in labeled ions (**II**) and (**IV**). With $^{18}O$ labeling, ion (**II**) $[^\bullet CH_2{}^{18}OH_2{}^+/OH_2]$, only shows loss of $H_2O$ in its mass spectra, indicating no positional interchange of the oxygen atoms. Furthermore, formation of protonated water is observed as a minor reaction for ion (**I**), absent for ion (**II**) and of medium importance for ion (**IV**) in the MI mass spectra. Upon collision, however, the $H_3O^+$ ion (or its isotopomers in labeled systems) increases in intensity for the ions (**I**) and (**II**) but remains almost unchanged for ion (**IV**).

To facilitate our discussion, a partial potential energy diagram is presented in Fig. 1. The relative energies of all four $CH_4O^{\bullet+}/H_2O$ ions and their dissociation products calculated at the G3 theory level are given in Tables 2 and 3, whereas Fig. 2 shows the calculated ground state geometry of ions (**I**) to (**IV**). The calculated energies of ions **I**, **II** and **IV**

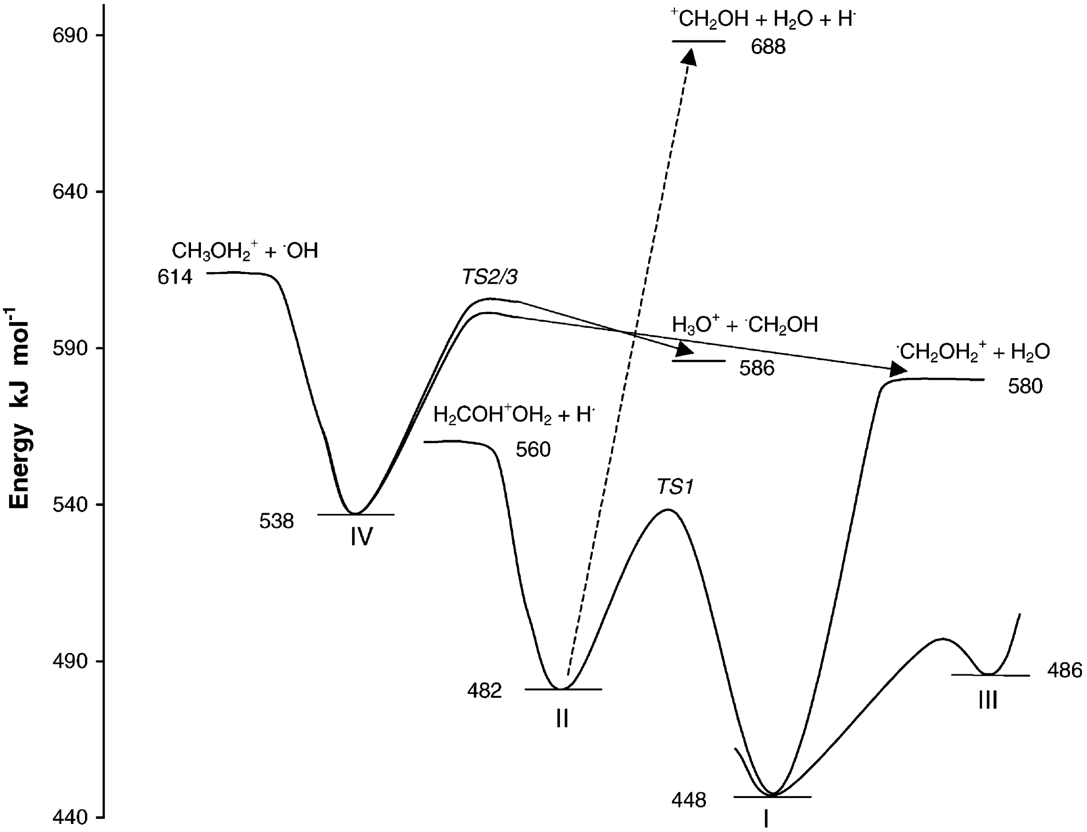

Fig. 1. Potential energy diagram for the $CH_4O^{\bullet +}/H_2O$ isomers (**I**) to (**IV**). The broken arrow is for a collision-induced dissociation. TS1 comes from [11b]; for TS2/3, see text.

Table 2
Calculated $\Delta_f H^\circ$(G3) values for ions and neutrals (kJ/mol)

| Species | $\Delta_f H^\circ$ |
|---|---|
| $^{\bullet}CH_2OH_2^+/OH_2$ (**I**) | 448 |
| $CH_3OH^{\bullet +}/OH_2$ (**II**) | 482 (482)[a] |
| $H_2O/HCH_2OH^{\bullet +}$ (**III**) | (486)[a] |
| $CH_3OH_2^+/OH^{\bullet}$ (**IV**) | 538 (536)[b] |
| $H_2COH^+/H_2O$ | 342 |
| $CH_3OH_2^+$ | 578 (574)[c] |
| $^{\cdot}CH_2OH_2^+$ | 821 (815)[c] |
| $CH_3OH^+$ | 850 (845)[c] |
| $^{\cdot}CH_2OH$ | −17 (−19)[c] |
| $H_3O^+$ | 603 (597)[c] |
| $H_2O$ | −241 (−242)[c] |
| OH | 36 (39)[c] |
| H | 218 |

[a] From ([11b] and reference therein).
[b] From [21].
[c] From [22].

are 448, 482 and 538 kJ/mol, respectively, in good agreement with those found by Gauld and Radom [11b]. Ion (**III**) can rearrange to (**I**) over only a small barrier of ca. 9 kJ/mol, while (**II**) occupies a potential well of depth 56 kJ/mol using the energy of TS1 given in [11]. The lowest energy dissociation channel, 112 kJ/mol above ion (**I**), is the loss of a hydrogen

Table 3
Calculated $\Delta_f H^\circ$(G3) values for dissociation products (kJ/mol)

| Species | $\Delta_f H^\circ$ |
|---|---|
| $^{\bullet}CH_2OH_2^+ + H_2O$ | 580 |
| $CH_3OH^{\bullet +} + H_2O$ | 609 |
| $CH_3OH_2^+ + {}^{\bullet}OH$ | 614 |
| $H_3O^+ + {}^{\bullet}CH_2OH$ | 586 |
| $CH_2OH^+/H_2O + H^{\bullet}$ | 560 |

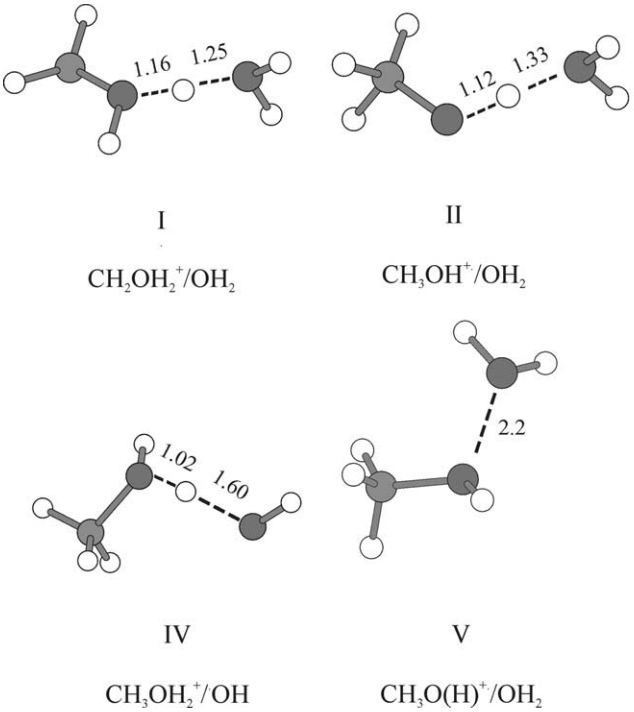

Fig. 2. Ground state structures for the isomeric $CH_4O^{\bullet+}/H_2O$ ions (**I**), (**II**), (**IV**) and (**V**).

atom to give $CH_2OH^+/OH_2$ (the proton bound formaldehyde/water ion), which is accessible to both ions (**I**) and (**II**). The next higher energy process is water loss to give rise to the distonic methanol ion, $^\bullet CH_2OH_2{}^+$, 132 kJ/mol above (**I**). Water loss to give the conventional methanol ion $CH_3OH^{\bullet+}$ would cost 30 kJ/mol more and therefore could not compete with the distonic ion. For ion (**I**), the water molecule can move freely about the $^\bullet CH_2OH_2{}^+$ moiety at energies below rearrangement to (**II**). Thus, the calculations [11], indicate that ions (**I**) and (**II**) should indeed be distinguishable by experiment.

The reactions of the three ions (**I**), (**II**) and (**IV**) observed experimentally can now be rationalized. With the relative positions for ions (**I**) and (**II**) and the transition state between them on the potential energy hyper-surface located by the theoretical calculations, a complete loss of positional identity of H/D atoms in (**I**) prior to water loss should be expected, and this is in accord with the experimental observation. As illustrated in the MI mass spectrum of $^\bullet CH_2O^+D_2/D_2O$, the (**I**)-$d_4$ ion, losses of $H_2O$, HDO and $D_2O$ were found in the ratio of 11:50:39 (the randomization ratio is 7:53:40). As discussed previously [13a], this experimental observation is different from those obtained from bimolecular reactions of the $^\bullet CH_2OH_2{}^+$ ion with $D_2O$ [9,10] where it was found that hydrogens attached to the oxygen of the distonic ion can exchange with water faster than those attached to carbon. Nevertheless, compared with the isolated methanol ions, where interconversion is prevented by the high energy barrier, it is confirmed that water catalyzes the reaction in such a way that the energy barrier is lowered sufficiently to allow free isomerization.

For ion (**II**)-$d_3$, $CH_3OD^{\bullet+}/D_2O$, the losses of $H_2O$, HDO and $D_2O$ were in the ratio of 41:43:16 (randomization gives 20:60:20), a result which cannot be fitted to any numbers of randomly participating H and D atoms. Thus, incomplete H/D mixing occurs prior to water loss, with a bias *against* loss of H/D attached initially to oxygen. Therefore, complete equilibration with (**II**) does not precede fragmentation. Note that these observations are in keeping with those for the bimolecular reactions between $^{\bullet}CH_2OH_2{}^{+}$ and a water molecule [10], where the $–^{+}OH_2$ hydrogen atoms were found to exchange with the substrate more rapidly than those attached to the carbon atom.

In contrast, the (metastable) ion (**IV**) consistently showed labeled water loss ratios corresponding most closely to the non-involvement of one methyl H or D, e.g., $CH_3OD_2{}^{+}/^{\bullet}OD$ has losses of $H_2O{:}HDO{:}D_2O = 11{:}52{:}36$, and for $CD_3OH_2{}^{+}/^{\bullet}OH$, the ratios are 34:57:9, in keeping with the involvement of 2H and 3D, and of 3H and 2D, respectively, and for which the random losses are in the ratio of 10:60:30 and 30:60:10, respectively. (Similar results were obtained for $CHD_2OH_2{}^{+}/^{\bullet}OH$, 53:44:∼3 and for $CHD_2OD_2{}^{+}/^{\bullet}OD$, 0:27:73, respectively.)

$H^{\bullet}$ (or $D^{\bullet}$) loss occurs for metastable (**I**) ions and it is biased towards loss of $H^{\bullet}$, possibly the result of an isotope effect. We propose that the rearrangement of ion (**I**) → (**II**) provides the reacting configuration for $H^{\bullet}$ loss, i.e., loss of a methyl H from (**II**) leads directly to the proton bound formaldehyde/water product ion. Note that this is the lowest energy dissociation process (Fig. 1). The necessity for this rearrangement to precede the loss of $H^{\bullet}$ explains the collision insensitivity of this reaction for (**I**).

For ion (**II**), $H^{\bullet}$ loss is almost exclusively from the methyl group in the MI and CID mass spectra, indicating that this reaction is kinetically more favorable than the isomerization. Ion (**IV**) is quite unlike (**I**) and (**II**); loss of a hydrogen atom is a minor reaction in both the MI and CID mass spectra.

It is noteworthy that upon collisional activation, a few other reactions are observed which are diagnostic for the three isomers. Formation of protonated methanol is a major product ion in the CID mass spectrum of ion (**IV**), of medium intensity in that of ion (**I**), and absent with ion (**II**). In addition, the $^{+}CH_2OH$ ion is observed in the CID mass spectra of ions (**I**) and (**II**).

It seems that ion (**IV**) must exist in a deep potential well, because no facile rearrangement to (**II**) (or further to (**I**)) is found, a process which would lead to a significant loss of $H^{\bullet}$ from metastable ions. Upon collision activation, ion (**IV**) loses $^{\bullet}OH$, a process which retains the H or D atom attached to oxygen. As discussed earlier, the H/D mixing preceding water loss is consistent with the participation of all label atoms *except one* attached initially to carbon (see above). A similar preference is observed for the production of $H_3O^{+}$ from (**IV**) for which it is solely a metastable ion process. This dissociation of the $CH_3O^{+}D_2/^{\bullet}OD$ and $CD_3O^{+}H_2/^{\bullet}OH$ ions yields only three hydronium ions, $D_3O^{+}$, $HD_2O^{+}$ and $H_2DO^{+}$ (no $H_3O^{+}$) for the former and $H_3O^{+}$, $H_2DO^{+}$ and $HD_2O^{+}$ (no $D_3O^{+}$) for the latter, both sets having a 1:3:1 abundance ratio. Again, one atom attached to C appears to be unable to participate, but in contrast to the water loss, the observed result is not that for either the randomization of 3D and 2H, or for 2D and 3H, respectively, 1:3:3 for the former, 3:3:1 for the latter. It is possible that a kinetic effect is responsible for these observations. If the barrier to the conversion of (**IV**) to its isomers is high enough, with the appropriate transition states TS2/3 (see Fig. 1) lying above the dissociation limits for $H_2O$ and $^{\bullet}CH_2OH$ losses, then complete positional equilibration of all H atoms prior to dissociation will be prevented.

Finally, yet another ion (**V**), represented as an electrostatically bound $^{+\bullet}O–O$ species, $CH_3O^{\bullet+}(H)OH_2$, see Fig. 2, has been found as a minimum at a high energy on the potential surface [20]. At the G3 level of theory we find (**V**) to lie at an energy of 552 kJ/mol.

The complexity of the chemistry of this simple system was not expected. Clearly, larger polyatomic ion/molecule pairs will be even more challenging, as we have found in the $CH_3CHO^{\bullet+}/H_2O$ system, which will be reported elsewhere.

## Acknowledgements

The authors thank Professors L. Radom and J.W. Gauld for valuable discussions and also the Natural Sciences and Engineering Research Council of Canada for continuing financial support.

## References

[1] J.L. Holmes, Org. Mass Spectrom. 20 (1985) 169.

[2] (a) W.J. Bouma, J.K. MacLeod, L. Radom, J. Am. Chem. Soc. 101 (1979) 5540;
(b) W.J. Bouma, D. Poppinger, S. Saebo, J.K. MacLeod, L. Radom, Chem. Phys. Lett. 104 (1984) 198;
(c) R.H. Nobes, W.J. Bouma, J.K. MacLeod, L. Radom, Chem. Phys. Lett. 135 (1987) 78.

[3] J.M. Buschek, J.L. Holmes, J.K. Terlouw, J. Am. Chem. Soc. 109 (1987) 7321.

[4] B.F. Yates, W.J. Bouma, L. Radom, J. Am. Chem. Soc. 109 (1987) 2250.

[5] D.K. Böhme, Int. J. Mass Spectrom. Ion Process. 115 (1992) 95.

[6] (a) A. Cunje, C.F. Rodriques, D.K. Böhme, A.C. Hopkinson, J. Phys. Chem. 102 (1998) 478;
(b) A. Cunje, C.F. Rodriques, D.K. Böhme, A.C. Hopkinson, Can. J. Chem. 76 (1998) 1138.

[7] (a) A.J. Chalk, L. Radom, J. Am. Chem. Soc. 119 (1997) 7573;
(b) A.L.L. East, B.J. Smith, L. Radom, J. Am. Chem. Soc. 119 (1997) 9014;
(c) A.J. Chalk, L. Radom, J. Am. Chem. Soc. 121 (1999) 1574.

[8] (a) L.M. Fell, P.C. Burgers, P.J.A. Ruttink, J.K. Terlouw, Can. J. Chem. 76 (1998) 335;
(b) P.J.A. Ruttink, P.C. Burgers, L.M. Fell, J.K. Terlouw, J. Phys. Chem. A 102 (1998) 2976;
(c) M.A. Trikoupis, J.K. Terlouw, P.C. Burgers, J. Am. Chem. Soc. 120 (1998) 12131;
(d) G. van der Rest, P. Mourgues, J. Tortajada, H.E. Audier, Int. J. Mass Spectrom. 179/180 (1998) 293;
(e) J. Chamot-Rooke, G. van der Rest, P. Mourgues, H.E. Audier, Int. J. Mass Spectrom. 195/196 (2000) 385;
(f) L.M. Fell, M.A. Trikoupis, J.K. Terlouw, Int. J. Mass Spectrom. 195/196 (2000) 85;
(g) M.A. Trikoupis, P.C. Burgers, P.J.A. Ruttink, J.K. Terlouw, Int. J. Mass Spectrom. 210/211 (2001) 489.

[9] H.E. Audier, D. Leblanc, P. Mourgues, T.B. McMahon, S. Hammerum, J. Chem. Soc. Chem. Commun. (1994) 2329.

[10] P. Mourgues, H.E. Audier, D. Leblanc, S. Hammerum, Org. Mass Spectrom. 28 (1993) 1098.

[11] (a) J.W. Gauld, H.E. Audier, J. Fossey, L. Radom, J. Am. Chem. Soc. 118 (1996) 6299;
(b) J.W. Gauld, L. Radom, J. Am. Chem. Soc. 119 (1997) 9831 (and references cited therein).

[12] T.D. Fridgen, J.M. Parnis, Int. J. Mass Spectrom. 190/191 (1999) 181.

[13] (a) Y.-P. Tu, J.L. Holmes, J. Am. Chem. Soc. 122 (2000) 3695;
(b) Y.-P. Tu, J.L. Holmes, J. Am. Chem. Soc. 122 (2000) 5597.

[14] J.L. Holmes, P.M. Mayer, J. Phys. Chem. 99 (1995) 1366.

[15] J.C. Traeger, A.A. Mommers, Org. Mass Spectrom. 22 (1987) 592.

[16] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.

[17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Ciolowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Resplogle, J.A. Pople, Gaussian 98 Rev. A. 7, Gaussian Inc., Pittsburgh, PA, 1998.

[18] L.A. Curtiss, K. Raghavachari, P.C. Refern, V. Rassolov, J.A. Pople, J. Chem. Phys. 109 (1998) 7764.

[19] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.

[20] A. Nicolaides, A. Rauk, M.N. Glukhovtsev, L. Radom, J. Phys. Chem. 100 (1996) 17460.

[21] J.W. Gauld, personal communication.

[22] W.G. Mallard, P.J. Lindstrom (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database No. 69, National Institute of Standards and Technology, Gaithersburg, MD, 1998.