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Water-Catalyzed Interconversion of Conventional and Distonic Radical Cations: Methanol and Methyleneoxonium Radical Cations

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It is now well established that conventional and distonic isomers of radical cations, e.g. methanol radical cation ($CH_3OH^{\bullet+}$, **1**) and methyleneoxonium radical cation ($\dot{C}H_2\overset{+}{O}H_2$, **2**), are often separated by a large barrier, resulting in their being individually observable.[2−4] Recently, however, Audier, Leblanc, Mourges, McMahon, and Hammerum[5] reported experiments which showed that interaction with a polar neutral molecule (e.g. water) can lead to facile interconversion of such isomeric ions, in contrast to the behavior of the isolated species. For example, $CH_3OH^{\bullet+}$ was observed to yield products characteristic of $\dot{C}H_2\overset{+}{O}H_2$ when produced in the presence of water. Audier et al.[5] noted that this could be considered an example of what Bohme had previously termed proton-transport catalysis.[6] In this communication, we use high-level ab initio calculations to provide a rationalization for the experimental observations.

Standard ab initio calculations[7] at a slightly modified level of G2 theory[8,9] were carried out with the Gaussian 92 and Gaussian 94 programs.[10] All relative energies reported in this paper refer to results at 0 K at this level of theory. Our calculated barrier for the conversion of isolated methanol radical cation (**1**) to methyleneoxonium radical cation (**2**) via transition structure (TS) **3** is 108 kJ mol^{-1}, and the energy difference between the isomers is 28.6 kJ mol^{-1} (Figure 1), very close to previous values at similarly high levels of theory[2d−f] and to an experimental estimate.[11] Note that the barrier to rearrangement is greater than the barrier to dissociation (66.2 kJ mol^{-1} via TS **4**) to give $CH_2OH^+ + H^\bullet$. This means that dissociation should take place preferentially to rearrangement in the isolated species.

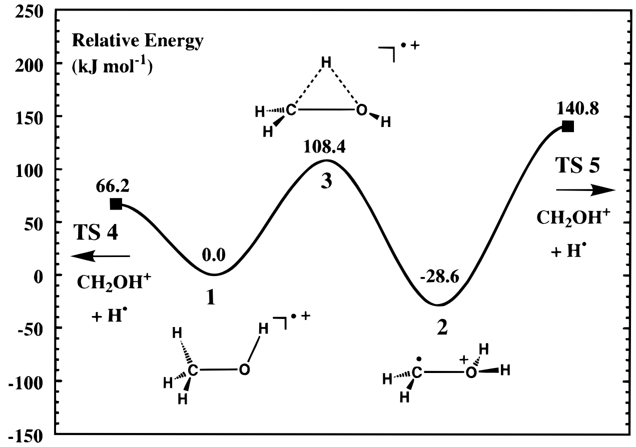

Figure 1. Schematic energy profile for the interconversion of the methanol radical cation (**1**) and the methyleneoxonium radical cation (**2**) (0 K, modified G2, see text).

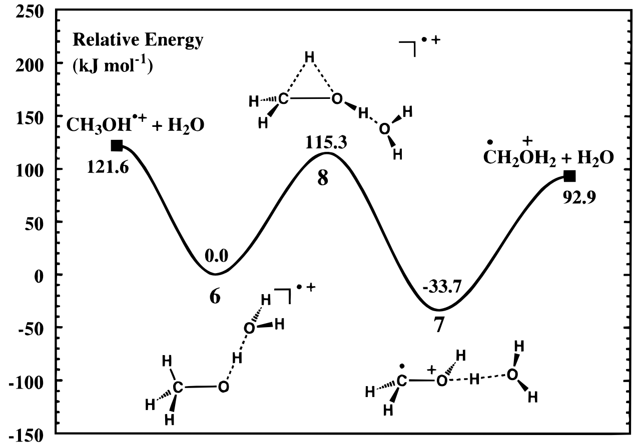

Figure 2. Schematic energy profile for the interconversion of the hydrated methanol radical cation (**6**) and the hydrated methyleneoxonium radical cation (**7**) involving a "spectator" O−H bound water molecule (0 K, modified G2, see text).

As a first step in examining the effect of the presence of water molecules on the rearrangement process, we considered a "spectator" water molecule, bound to the hydroxyl hydrogen throughout. This might be regarded as the transformation of hydrated methanol radical cation (**6**) to hydrated methyleneoxonium radical cation (**7**) via TS **8** (Figure 2) and has been investigated previously by Burcl and Hobza.[12] We find that the barrier to the transformation actually increases slightly, from 108 to 115 kJ mol^{-1}, as a result of the complexation with a

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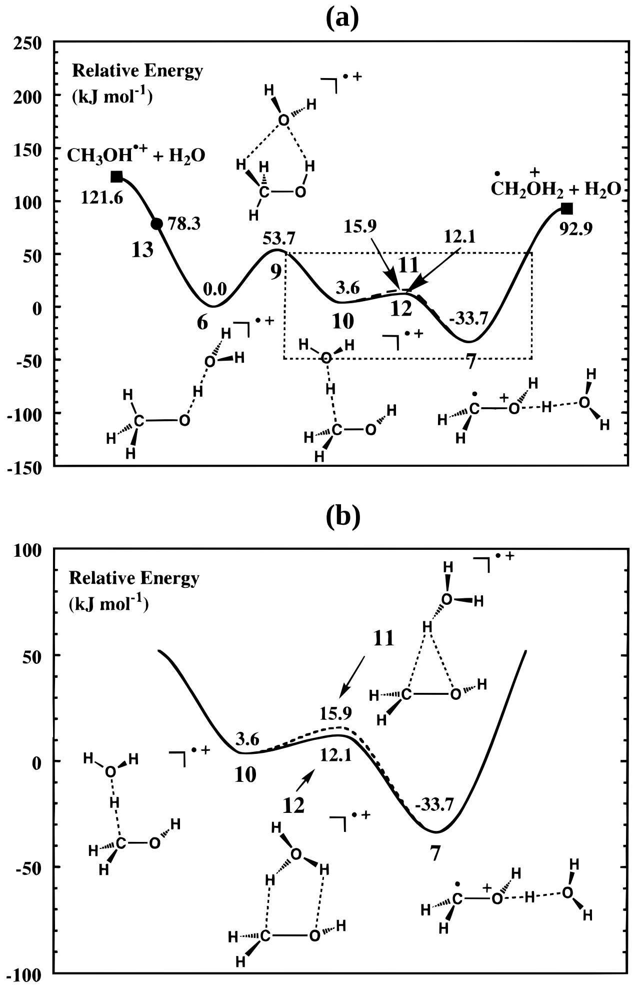

Figure 3. (a) Schematic energy profile for the preferred water-catalyzed interconversion of the methanol radical cation and methyleneoxonium radical cation involving O−H-hydrated (**6**, **7**) and C−H-hydrated (**10**) species. (b) Inset from (a) showing in more detail the interconversion of the C−H-hydrated methanol radical cation (**10**) and the O−H-hydrated methyleneoxonium radical cation (**7**) (0 K, modified G2, see text).

single water molecule. On the other hand, the rearrangement TS **8** lies slightly lower in energy than separated $CH_3OH^{\bullet+} + H_2O$.

A more effective involvement of the water molecule is found for the two pathways shown in Figure 3. The hydrated methanol radical cation in which water is bound to the hydroxyl hydrogen (**6**) may be formed either by interaction of methanol radical cation with water or by ionization of a methanol−water dimer or larger cluster. Migration of water from the O−H hydrogen to a C−H hydrogen can take place via TS **9** at a cost of 53.7 kJ mol^{-1}, producing the C−H-hydrated methanol radical cation **10**. This complex could also be formed directly starting from $CH_3OH^{\bullet+}$ and H_2O. The C−H···OH_2 bonded complex **10** can then rearrange to the hydrated methyleneoxonium radical cation **7** in two ways (Figure 3b). In the first, the water "drags" the C−H hydrogen across the C−O bond, via TS **11** lying just 12.3 kJ mol^{-1} above **10**, to produce **7**. An alternative pathway from **10** to **7** involves the five-membered cyclic TS **12** and a barrier of 8.5 kJ mol^{-1}, even lower than that for rearrangement via **11**. An important point is that this latter pathway results in the exchange of internal and external protons. The water molecule is well placed to facilitate the rearrangement of methanol radical cation to methyleneoxonium radical cation because its proton affinity (calculated value of 682 kJ mol^{-1} at 0 K) is greater than the proton affinity of $CH_2OH^{\bullet}$ at carbon (661 kJ mol^{-1}) but less than the proton affinity of $CH_2OH^{\bullet}$ at oxygen (690 kJ mol^{-1}). We note that the energies of the transition structures **11** and **12** are considerably lower than that of separated $CH_3OH^{\bullet+} + H_2O$ and are also lower than that of the TS (**13**) for dissociation to $CH_2OH{\cdots}OH_2^{\bullet+} + H^{\bullet}$ (78.3 kJ mol^{-1}). Thus, the single water molecule has very effectively allowed the transformation of methanol radical cation to its distonic isomer.

Finally, we note that deuterium-labeling experiments[5] show that two of the four hydrogens of $CH_3OH^{\bullet+}$ can exchange readily with the external water molecule whereas the other two hydrogens exchange more slowly. Our calculations provide a straightforward rationalization for these observations. We have already seen that conversion of **10** to **7** via **12** results in exchange of one of the carbon-bound hydrogens with a hydrogen of the external water molecule. We find in addition that migration of a water molecule between the two oxygen-bound protons in **7** can take place at an energy 45.6 kJ mol^{-1} above **7**.[13] Scrambling of the two oxygen-bound hydrogens in **7** can then be achieved either by revisiting isomer **10** and rearrangement within **10**, predicted to require 45.8 kJ mol^{-1}, or via further rearrangement within **7**, predicted to require 57.2 kJ mol^{-1}.[13] On the other hand, the barrier to "returning" from **7** to **6** via TS **9**, which would be necessary for the exchange of the other two carbon-bound hydrogens, is substantially greater (87.4 kJ mol^{-1}). Thus, our calculations predict that one of the original carbon-bound hydrogens plus the oxygen-bound hydrogen of $CH_3OH^{\bullet+}$ exchange readily whereas exchange of the other two carbon-bound hydrogens is more difficult, consistent with the experimental observations.

In summary, conversion of the isolated methanol radical cation (**1**) to the methyleneoxonium radical cation (**2**) requires 108 kJ mol^{-1} (Figure 1). If a "spectator" water molecule is bound to the hydroxyl hydrogen, the barrier for the transformation of the hydrated methanol radical cation **6** to the hydrated methyleneoxonium radical cation **7** is actually increased slightly to 115 kJ mol^{-1} (Figure 2), but the TS for this rearrangement lies slightly below the energy of separated $CH_3OH^{\bullet+} + H_2O$. The best water-catalyzed transformations, involving in particular a C−H-hydrated species **10**, occur well below the energy of separated $CH_3OH^{\bullet+} + H_2O$ (Figure 3). The water-catalyzed transformation of methanol radical cation to methyleneoxonium radical cation does indeed represent an elegant example of proton-transport catalysis.

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