Available online at www.sciencedirect.com
SCIENCE DIRECT®

International Journal of Mass Spectrometry 242 (2005) 49–56

www.elsevier.com/locate/ijms

The acid-catalyzed rearrangement $CH_3O^\bullet \rightarrow {}^\bullet CH_2OH$ and its involvement in the dissociation of the methanol dimer radical cation A Quid pro Quo reaction

Peter C. Burgers[a], Paul J.A. Ruttink[b,*]

[a] Laboratory for Neuro-Oncology, Department of Neurology, Erasmus MC, P.O. Box 1738, 3000 DR Rotterdam, The Netherlands
[b] Theoretical Chemistry Group, Department of Chemistry, University of Utrecht, 3584 CH Utrecht, The Netherlands

Received 20 August 2004; accepted 8 November 2004
Available online 29 December 2004

Abstract

The barrier for the **radical** isomerization $CH_3O^\bullet \rightarrow {}^\bullet CH_2OH$ is calculated by CBS-QB3 to be 29.7 kcal mol^{-1} and lies higher (by 5.7 kcal mol^{-1}) than the dissociation limit $CH_2O + H^\bullet$. Hence, $CH_3O^\bullet$ does not isomerize to the more stable ${}^\bullet CH_2OH$ on its own. However, this barrier is reduced to 15.8 kcal mol^{-1} when the $CH_3O^\bullet$ radical is coordinated with protonated methanol ($CH_3{-}O^\bullet \cdots H{-}O(H){-}CH_3{}^+$) and the $CH_3O^\bullet \rightarrow {}^\bullet CH_2OH$ rearrangement can now take place within the complex. This rearrangement, which results in the hydrogen-bridged radical cation ${}^\bullet CH_2{-}O(H)\cdots H{-}O(H){-}CH_3{}^+$ can be viewed as an acid-catalyzed rearrangement. The ion $CH_3{-}O^\bullet \cdots H{-}O(H){-}CH_3{}^+$ represents the most stable form of the methanol dimer radical cation. The ion ${}^\bullet CH_2{-}O(H)\cdots H{-}O(H){-}CH_3{}^+$ can fragment directly to $CH_3OH_2{}^+ + {}^\bullet CH_2OH$ or it can rearrange further to produce the hydrogen-bridged radical cation ${}^\bullet CH_2{-}O^+(CH_3){-}H\cdots OH_2$, which is the dimethylether ylid cation solvated by water. This species can dissociate to its components or to $CH_2{=}O\cdots H^+\cdots OH_2 + CH_3{}^\bullet$ via an S_N2 type reaction. Alternatively, ${}^\bullet CH_2{-}O^+(CH_3){-}H\cdots OH_2$ may undergo "proton-transport catalysis" to produce the complex ion $CH_3{-}O{-}CH_3{}^{\bullet +}\cdots OH_2$ which then dissociates. Our calculations confirm for the most part recent experimental findings on the methanol dimer radical cation [Y.-P. Tu, J.L. Holmes, J. Am. Chem. Soc. 112 (2000) 3695] but they also provide a different mechanism for the key isomerization reaction observed in that study.

Keywords: Proton-transport catalysis; Dimer radical cation; Solvated distonic ions; Ab initio calculations; Acid-catalyzed rearrangement

1. Introduction

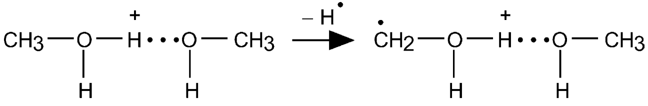
Since their discovery in 1982, distonic ions [1] have been the subject of many studies with the aim of gaining insight into their intrinsic properties, such as their thermodynamic stabilities and their barriers towards rearrangements into their better known conventional isomers. For example, it was found by theory [2] and experiment [3] that the prototype distonic ion ${}^\bullet CH_2OH_2{}^+$ is more stable than its isomer $CH_3OH^{\bullet +}$, but a significant barrier towards this 1,2-hydrogen atom shift prevents transformation. However, if this distonic ion is coordinated with an appropriate solvent molecule, the barrier towards isomerization may completely disappear by a process called "proton-transport catalysis" (PTC) [4]. Thus, production of the distonic ion from ionized methanol may be catalyzed by water [3b,e,f]. Solitary distonic ions can be produced in the rarefied gas-phase by judiciously chosen dissociative ionizations, but production of a distonic ion associated with a single solvent molecule appears much more difficult. This is true even for ion cyclotron resonance (ICR) experiments [5] which allow the study of association reactions of distonic ions. Recently, Tu and Holmes [6] presented an elegant method to produce (formally) solvated distonic ions from more or less readily available proton-bound molecule pairs using a tandem mass spectrometer. In this technique, the solvated distonic ion is produced by the collisional-induced loss of a radical from the proton-bound molecule pair. For example the putative complex-ion ${}^\bullet CH_2OH_2{}^+/CH_3OH$, **1**, was generated

---

* Corresponding author.
E-mail address: p.j.a.ruttink@chem.uu.nl (P.J.A. Ruttink).

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.11.006

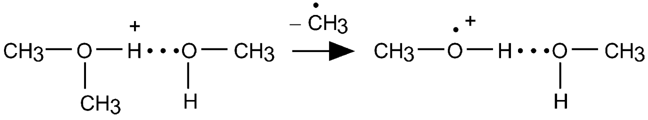
according to:



$$CH_3-\underset{H}{O}-\overset{+}{H}\cdots\underset{H}{O}-CH_3 \xrightarrow{-H^\bullet} \overset{\bullet}{C}H_2-\underset{H}{O}-\overset{+}{H}\cdots\underset{H}{O}-CH_3$$

1

Isotopic labeling is necessary to identify the $H^\bullet$ atom lost. It was observed that ions **1** dissociate via three channels to produce $CH_3OH_2^+ + CH_2OH^\bullet$, ${}^\bullet CH_2–O^+(H)–CH_3 + H_2O$ and $CH_2{=}O\cdots H^+\cdots OH_2 + CH_3^\bullet$. The isomeric methanol$^{\bullet+}$/methanol dimer radical cation was also formed using the above technique, according to:



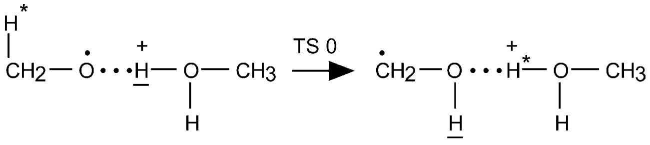
$$CH_3-\underset{CH_3}{O}-\overset{+}{H}\cdots\underset{H}{O}-CH_3 \xrightarrow{-{}^\bullet CH_3} CH_3-\overset{\bullet +}{O}-H\cdots\underset{H}{O}-CH_3$$

2

Again, isotopic labeling is necessary to identify the $CH_3^\bullet$ radical lost. (Dimer radical cations can also be produced by ICR via ligand exchange reactions of $Xe_2^{\bullet+}$ [4h]) Ions **2** dissociate to the same products as ions **1**, and so, **1** and **2** may communicate prior to dissociation. Based on thermochemical arguments, kinetic considerations and isotopic labeling experiments, Tu and Holmes derived a reaction profile for the interconversion and dissociations of **1** and **2**. Particularly interesting observations pertain to labeling experiments. From such experiments, Tu and Holmes [6] concluded that only the hydrogen atoms of the *ionic* partner in **2** become positionally equivalent prior to the formation of $CH_3OH_2^+ + CH_2OH^\bullet$. By contrast, the hydrogen atoms in the ionic partner of **1** do *not* lose their positional identity prior to this dissociation. Consider the reaction sequence:

$$
\begin{aligned}
&CH_3–O–H^{\bullet+}\cdots O(H)–CH_3\ (\mathbf{2})\\
&\to \text{TS 0} \to {}^\bullet CH_2–O(H)–H^+\cdots O(H)–CH_3\ (\mathbf{1})\\
&\to \text{TS 1} \to {}^\bullet CH_2–O(H)\cdots H^+–O(H)–CH_3\\
&\to CH_2OH^\bullet + CH_3OH_2^+
\end{aligned}
$$

where TS 1 represents a proton shift. If TS 0 lies higher in energy than the dissociation limit $CH_2OH^\bullet + CH_3OH_2^+$ (and also higher than TS 1), then the H/D randomization reactions via **2** ↔ **1** can only occur when starting from ions **2**; in the above scenario ions **1** formed directly will not communicate with **2** but will dissociate. This interconversion can be considered as a PTC, where the neutral methanol molecule acts as the base, but it was observed that the proton affinities (PA) of the species involved do not meet Radom's PA criterion [4f] for successful PTC. According to this criterion, the PA of the base should lie between the PA of ${}^\bullet CH_2OH$ at O (160 kcal mol^{-1}) and at C (167 kcal mol^{-1}, PA values taken or calculated from ref. [7], using the revised value for $\Delta H_f\,[{}^\bullet CH_2OH] = -4$ kcal mol^{-1} [8]), but the PA of methanol (182 kcal mol^{-1}) is much larger. It has been observed that Radom's criterion can be extended downwards to include bases of lower PA, but not upwards [4s,t]. It was proposed that the transformation **2** → **1** should instead be viewed as an intraionic 1,2-hydrogen *atom* shift [6], perhaps via a spectator mechanism [4e,f,j]. Tu and Holmes also mentioned that high-level theoretical calculations would be required to provide a definitive description of the reaction mechanism involved to which we now make a contribution. Our calculations indicate that ion **1** is not a minimum but a transition state for a degenerate isomerization and that ion **2** is a high energy structure lying in a shallow well only. Furthermore, and as surmised by Tu and Holmes [6], TS 1 does not appear to exist. The above transformation (i.e., **2** → **1**) can best be viewed as the *acid*-catalyzed rearrangement $CH_3O^\bullet \to {}^\bullet CH_2OH$, i.e., **3** → **4** as shown below:



$$\overset{H^*}{CH_2}-\overset{\bullet}{O}\cdots\overset{+}{\underline{H}}-\underset{H}{O}-CH_3 \xrightarrow{\text{TS 0}} \overset{\bullet}{C}H_2-\underset{\underline{H}}{O}\cdots\overset{+}{H^*}-\underset{H}{O}-CH_3 \qquad (1)$$

3 **4**

In this mechanism, the bridging proton (<u>H</u>) moves over to the $CH_3O^\bullet$ radical and at the same time the $CH_3OH^{\bullet+}$ rotates and donates a proton (H*) to the oxygen atom of its neutral CH_3OH partner. This reaction can best be viewed as a Quid pro Quo type of catalyzed isomerization [4r,9]. Our calculations offer an alternative interpretation for the labeling experiments by Tu and Holmes [6] and provide further insight into the dissociation behavior of species **3** and **4**.

2. Theoretical methods

The calculations were performed using GAMESS-UK [10] and Gaussian 98 revision A.9 [11]. The standard CBS-QB3 [12] model chemistry was used to probe the structures and energies of isomeric molecules and cations. Spin contaminations were within acceptable range (<0.8), except for TS 6 for which $\langle S^2\rangle = 0.916$.

Our calculations are summarized in Tables 1–3 and the associated energy diagram is shown in Fig. 1. The TS structures are shown in Scheme 1. The TS numbering follows that of ref. [6]. As argued by Tu and Holmes, an upper limit of the internal energy available to the metastable ions can be deduced. First, formation of $CH_3OCH_2^\bullet + H_3O^+$ is not observed and this places the upper limit at 143.1 kcal mol^{-1}. Secondly, the kinetic energy releases of all reactions are rather small and so the internal energy cannot lie far above the highest TS, i.e., TS 2. We estimate the metastable ions to dissociate between 135 and 140 kcal mol^{-1}. This precludes the production of $CH_3OH_2^+ + CH_3O^\bullet$ vis a vis $CH_3OH_2^+ + CH_2OH^\bullet$ [6].

3. Results and discussion

3.1. The structure of the $CH_3OH^{\bullet+}/CH_3OH$ complex

An encounter of $CH_3OH^{\bullet+}$ with a neutral CH_3OH molecule leads to the stable structure **3**,

Table 1
Electronic energies (hartree), vibrational energies (kcal mol^{-1}), and heats of formation (kcal mol^{-1}) for various isomers and transition states for the $CH_3OH^{\bullet+}/CH_3OH$ system

Species	B3LYP/CBSB7	ZPVE	CBS-QB3	ΔH_f/298 K
2 $CH_3OH^{\bullet+}/CH_3OH$	−231.18612	65.1	−230.71822	129.0
3 $CH_3{-}O^{\bullet}\cdots H{-}O(H){-}CH_3^{+}$	−231.19414	63.4	−230.73774	116.8
4 $^{\bullet}CH_2{-}O(H)\cdots H{-}O(H){-}CH_3^{+}$	−231.20183	64.1	−230.75140	108.4
5 $^{\bullet}CH_2{-}O^{+}(CH_3){-}H\cdots OH_2$	−231.20499	63.6	−230.75757	104.6
6 $CH_3{-}O{-}CH_2{-}H^{\bullet+}\cdots OH_2$	−231.19767	62.9	−230.74047	115.2
TS 0	−231.17655	63.3	−230.71208	132.6
TS 2	−231.16156	62.6	−230.71042	134.4
TS Spectator	−231.14050	60.9	−230.69379	144.2
TS 3	−231.18099	63.4	−230.71312	132.2
TS 4a	−231.18776	64.6	−230.73758	116.9
TS 4b	−231.17611	64.6	−230.72544	124.3
TS 5	−231.18010	63.7	−230.73411	118.8
TS 6	−231.17780	61.3	−230.72235	126.9
TS 7	−231.11742	59.8	−230.66954	159.7
TS 8	−231.15725	62.7	−230.70024	140.5

Table 2
Dissociations limits (kcal mol^{-1}) for the $CH_3OH^{\bullet+}/CH_3OH$ system

		ΔH_f/298 K
$CH_2O\cdots H\cdots OH_2^{+}$	$+CH_3^{\bullet}$	116.4
$CH_3OCH_3^{\bullet+}$	$+H_2O$	127.7
$CH_2O(H)CH_3^{\bullet+}$	$+H_2O$	131.4
$CH_3OH_2^{+}$	$+CH_2OH^{\bullet}$	133.5
$CH_3OH_2^{+}$	$+CH_3O^{\bullet}$	142.0
$CH_2OCH_3^{\bullet}$	$+H_3O^{+}$	143.1

$CH_3{-}O^{\bullet}\cdots H{-}O(H){-}CH_3^{+}$, that is to say, the O–H proton spontaneously moves over to the neutral methanol. The ion $CH_3OH^{\bullet+}/CH_3OH$, **2,** see also Scheme 1, does represent an equilibrium structure, but it lies 12.2 kcal mol^{-1} higher than **3** with a barrier separating it from **3** of only 3.2 kcal mol^{-1}. Thus, the methanol dimer radical cation $CH_3OH^{\bullet+}/CH_3OH$ lies in a shallow well only. That the proton attaches itself more closely to the methanol molecule as opposed to the $CH_3{-}O^{\bullet}$ radical also follows from the relative proton affinities: PA[CH_3OH] = 182 kcal mol^{-1}, PA[$CH_3O^{\bullet}$] = 169 kcal mol^{-1} [6,7].

3.2. Structure and formation of the $CH_2OH_2^{\bullet+}/CH_3OH$ complex

Our calculations indicate that ions **3** can isomerize via TS0 to the very stable species $^{\bullet}CH_2{-}O(H)\cdots H{-}O(H){-}CH_3^{+}$, **4**, according to Eq. (1). The structure of TS 0 is given in Scheme 1. The $CH_3OH_2^{+}$ moiety in **3** donates an O–H proton to the oxygen atom of $CH_3O^{\bullet}$ and at the same time, the incipient $CH_3OH^{\bullet+}$ radical cation donates back a C–H proton to produce **4** via TS 0. This transformation can be viewed as the *acid*-catalyzed radical rearrangement $CH_3O^{\bullet} \rightarrow {}^{\bullet}CH_2OH$ where the acid is the protonated methanol; in this reaction one of the $CH_3O^{\bullet}$ hydrogen atoms in **3** ends up as the hydrogen bridge in **4**, see Eq. (1). Unassisted this reaction has a barrier of 29.7 kcal mol^{-1} (CBS-QB3, this work) but catalysis by $CH_3OH_2^{+}$ reduces this barrier to 15.8 kcal mol^{-1}, corresponding to TS 0. Note that the first proton transfer is not followed by dissociation to $CH_3OH^{\bullet+} + CH_3OH$ as these products lie prohibitively high (see Fig. 1). We have also considered formation of **4** directly from **2** via a so-called “spectator” mechanism [4e,f,j]. However, the calculated en-

Table 3
Heats of formation (ΔH_f), reaction energies (RE), reverse activation energies (RAE) and activation energies (E_{act}) for species encountered on the $CH_3OH^{\bullet+}/CH_3OH$ potential energy surface

Reactant (R) → products (P)	ΔH_f (R)	ΔH_f (TS)	ΔH_f (P)	RE[a]	RAE[b]	E_{act}[c]
$CH_2OH_2^{\bullet+} \rightarrow CH_2OH^{+} + H^{\bullet}$	196.5	236.1	221.2	24.7	14.9	39.6
$CH_2O(H)CH_3^{\bullet+} \rightarrow CH_2OH^{+} + CH_3^{\bullet}$	189.7	209.6	204.6	14.9	5.0	19.9
$CH_2O(H)CH_3^{\bullet+} \rightarrow CH_2OCH_3^{+} + H^{\bullet}$	189.7	229.0	212.1	22.4	16.9	39.3
$CH_2OH_2^{\bullet+}\cdots OH_2 \rightarrow CH_2O{-}H^{+}\cdots OH_2 + H^{\bullet}$	106.8	147.4	133.0	26.2	14.4	40.6
$CH_2O(CH_3)H^{\bullet+}\cdots OH_2 \rightarrow CH_2O{-}H^{+}\cdots OH_2 + CH_3^{\bullet}$	104.6	126.9	116.4	11.8	10.5	22.3
$CH_2O(CH_3)H^{\bullet+}\cdots OH_2 \rightarrow CH_2OCH_3^{+}\cdots OH_2 + H^{\bullet}$	104.6	159.7	139.7	35.1	20.0	55.1
$CH_2O(CH_3)H^{\bullet+} \rightarrow CH_3OCH_3^{\bullet+}$	189.7	220.2	186.0	−3.7	34.2	30.5
$CH_2O(CH_3)H^{\bullet+}\cdots OH_2 \rightarrow CH_3OCH_3^{\bullet+}\cdots OH_2$	104.6	118.8	115.2	10.6	3.6	14.2

All values in kcal mol^{-1} from CBS-QB3 calculatons. ΔH_f ($H^{\bullet}$) = 52.1 kcal mol^{-1}. ΔH_f ($CH_3^{\bullet}$) = 35.5 kcal mol^{-1}.

[a] RE = ΔH_f (P) − ΔH_f (R).

[b] RAE = ΔH_f (TS) − ΔH_f (P).

[c] $E_{act} = \Delta H_f\,(TS) - \Delta H_f\,(R)$ = RE + RAE.

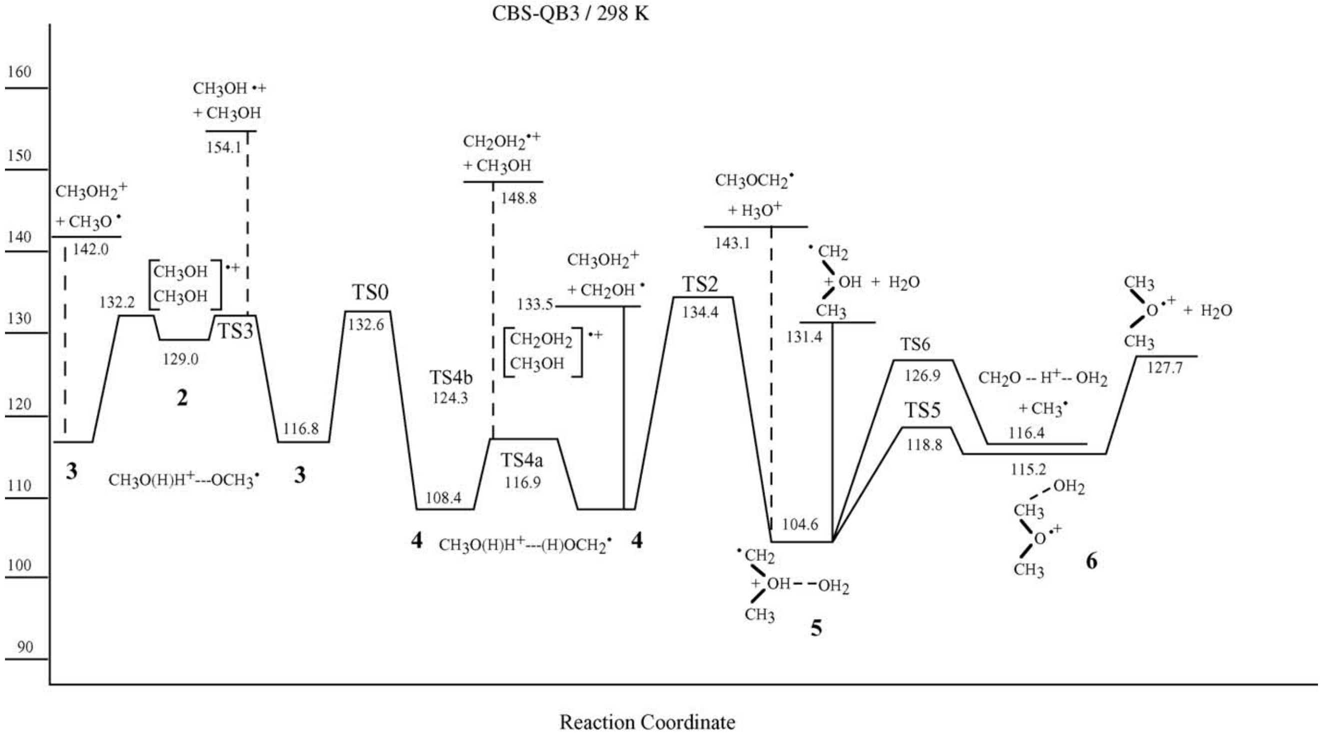
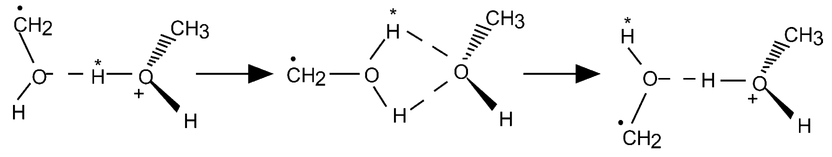


Fig. 1. Energy level diagram (CBS-QB3/298K, kcal mol^{-1}) for the dissociations of the methanol dimer radical cation.

ergy of the associated TS (144.2 kcal mol^{-1}; see Table 1 and for structure see Scheme 1) lies above the metastable window (see Fig. 1) and so a spectator mechanism can be ruled out. As expected for a spectator mechanism the barrier for this process (27.4 kcal mol^{-1}) is similar to the barrier for the unassisted reaction (29.7 kcal mol^{-1}).

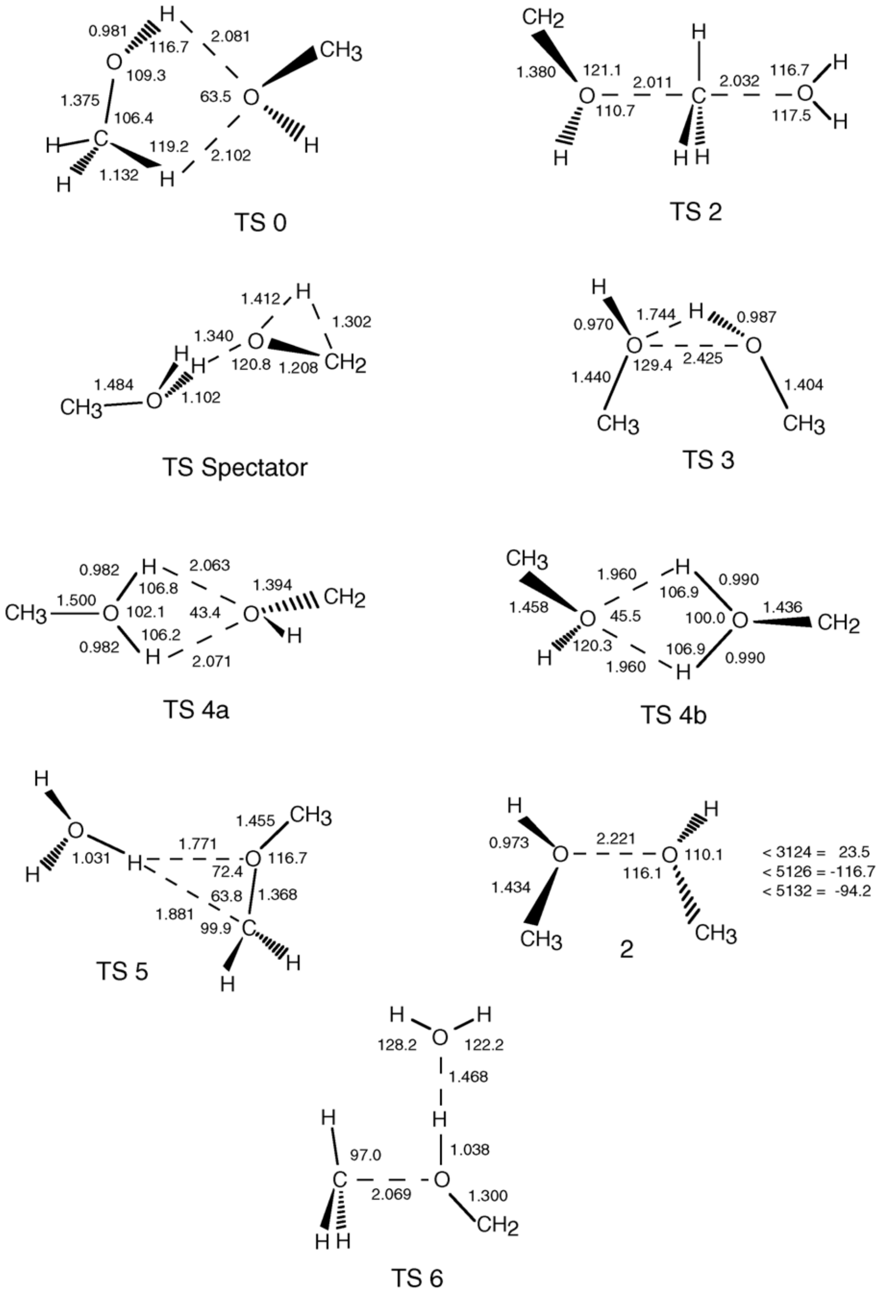
*3.3. Degenerate isomerizations of **4**: H/D exchange reactions*

Ions **4** may undergo two degenerate isomerizations. In the first the $CH_3OH_2^+$ partner in **4** rotates such that its other O–H hydrogen becomes the bridge. This TS (TS 4a, see Scheme 1) lies at 116.9 kcal mol^{-1}. In another mechanism, the bridging proton in **4** moves to the $^•CH_2OH$ partner and at the same time the incipient $^•CH_2OH_2^+$ rotates and donates back its other O–H hydrogen, see below:



4 TS 4b **4**

The associated TS (TS 4b) lies at 124.3 kcal mol^{-1}. By these degenerate isomerizations, all oxygen-bonded hydrogens in **4** can become positionally equivalent. Tu and Holmes [6] observed that their labeled complex $CH_3OD^{•+}/CD_3OD$, **2**, forms CD_3OHD^+ and $CD_3OD_2^+$ in a ratio of 3:1 which they took, quite reasonably, as showing that the H and D atoms in the ionic partner $CH_3OD^{•+}$ become positionally equivalent via the reversible isomerization **2** ↔ **1** (and one of these, either as a proton (H^+) or a deuteron (D^+), moves over to the neutral CD_3OD moiety). However, since $^•CH_2OH_2^+/CH_3OH$ is not an equilibrium structure, but rather a transition state for a degenerate isomerization, see above, it cannot be responsible for the observed H/D equilibration reactions. In our mechanism and starting from $CH_3–O^•\cdots D–O(D)–CD_3^+$, **3**, an irreversible isomerization via TS 0 leads to $^•CH_2–O(D)\cdots H–O(D)–CD_3^+$, **4**. Next, in the degenerate isomerizations **4** ↔ **4**, all three H and D atoms attached to both oxygen atoms become positionally equivalent, and *two* of these appear in the product ion and so in the absence of an isotope effect we predict a ratio of 2:1 for formation of CD_3OHD^+ and $CD_3OD_2^+$. Our calculations provide an explanation for the observation that the ion $CH_2OD_2^{•+}/CH_3OD$ (which actually is $^•CH_2–O(D)\cdots D–O(D)–CH_3^+$) does not show any H/D mixing [6]. This we argue is because in the degenerate exchange mechanisms above, all exchangeable atoms are already deuterium atoms.



Scheme 1. Geometries of the transition states encountered on the $CH_3OH^{\bullet +}/CH_3OH$ potential energy surface. Ion 2 is the equilibrium structure of the methanol dimer radical cation.

3.4. *Mechanism of isomerization* **4** $\rightarrow$ **5***: an* S_N2 *reaction* [6]

Proceeding further on the potential energy surface, ions **4** may rearrange via TS 2 to the complex $^{\bullet}CH_2–O^+(CH_3)–H\cdots OH_2$, **5**. This is a hydrogen-bridged complex of the distonic ion $^{\bullet}CH_2–O^+(H)–CH_3$ and H_2O and truly represents a solvated distonic ion. This ion represents the global minimum. As argued by Tu and Holmes [6] and by others for different systems [13] this reaction involves breaking of the hydrogen bond in $^{\bullet}CH_2–O(H)\cdots H–O(H)–CH_3^+$ after which the $CH_3OH_2^+$ partner can freely rotate within the dipole field of the $^{\bullet}CH_2OH$ radical. Next, backside nucleophilic displacement leads to TS 2, $^{\bullet}CH_2–O(H)\cdots CH_3^+\cdots OH_2$, where a methyl cation is coordinated with water and $^{\bullet}CH_2OH$ on each side. Next, the methyl cation moves towards the oxygen atom of $^{\bullet}CH_2–O(H)$ and subsequent hydrogen bridging leads to $^{\bullet}CH_2–O^+(CH_3)–H\cdots OH_2$, **5**. In agreement with ref. [6], we find that TS 2 represents the rate-determining step.

3.5. *Dissociations of ion* **5**

The complex ion **5** has a number of options. First, it can dissociate directly into its components, the ylid ion $^{\bullet}CH_2-O^+(CH_3)-H + H_2O$. Secondly, it can lose $CH_3^{\bullet}$ to produce the proton-bound molecule pair $CH_2=O\cdots H^+\cdots OH_2$, precisely as observed by Tu and Holmes [6]. (The ion $CH_2=O\cdots H^+\cdots OH_2$ is also formed by loss of $CH_3^{\bullet}$ from the unrelated complex ion $CH_3CH_2OH^{\bullet+}/H_2O$ [4g].) Loss of $CH_3^{\bullet}$ from **5** involves the cleavage of an O–C bond and as can be seen from Table 3, this reaction has a significant reverse term (TS6), paralleling the behavior of non-solvated distonic ions [14]. Interestingly, the reverse activation energy for the solvated ion (10.5 kcal/mol) is twice that of the bare ion (5.0 kcal mol^{-1}, see Table 3). Loss of $H^{\bullet}$ from ion **5** to generate $CH_3OCH_2^+\cdots OH_2$ is thermodynamically just possible at $\Sigma\Delta H_f = 139.7$ kcal mol^{-1} (see Table 3) but this reaction has an even larger reverse activation energy (20.0 kcal mol^{-1} via TS 7; see Tables 1 and 3) and so loss of $H^{\bullet}$ is not observed at all. There is a fourth option open to ions **5** and this is proton-transport catalysis (PTC) within the complex ion via TS 5. This rearrangement produces $CH_3-O-CH_3^{\bullet+} + H_2O$ via the complex ion $CH_3-O-CH_2-H^{\bullet+}\cdots OH_2$, **6**. (The PAs of $^{\bullet}CH_2-O-CH_3$ at O and C are 173 and 176 kcal mol^{-1} (from ref. [7] and ΔH_f [$^{\bullet}CH_2-O^+(H)-CH_3$] = 189.7 kcal mol^{-1}, this work, Table 3), whereas PA[H_2O] = 166 kcal mol^{-1} so that PTC is possible.) The barrier for the reaction **5** → **6** is 14.2 kcal mol^{-1} (most of which represents the reaction's endothermicity) which is considerably lower than that for the bare ion (30.5 kcal mol^{-1}, see Table 3). Experimentally it is found that loss of water is associated with H/D exchange reactions, but by contrast loss of a methyl radical is atom specific. For example, the ion $^{\bullet}CH_2-O^+(CH_3)-D\cdots OD_2$ (**5**) formed from $^{\bullet}CH_2-O(D)\cdots D-O(D)-CH_3^+$ (**4**) via the rate-determining step TS 2 dissociates by loss of $CH_3^{\bullet}$ and D_2O (as expected) but it also abundantly loses HDO (see Fig. 1c in ref. [6]). However, vide supra, formation of $CH_3OD_2^+$ is atom specific. It could be argued that starting from ions **4,** the reversible isomerization **4** to **3** (which would lead to H/D exchange in $CH_2-O(D)\cdots D-O(D)-CH_3^+$) occurs prior to the loss of water, but not prior to formation of $CH_3OH_2^+ + CH_2OH^{\bullet}$. However, exchange reactions are seen for both losses of H_2O and $^{\bullet}CH_2OH$ when starting from **3**. The above is possible if TS 0 (132.6 kcal mol^{-1}) lies below TS 2 (134.4 kcal mol^{-1}) and if the level for $CH_3OH_2^+ + CH_2OH^{\bullet}$ (133.5 kcal mol^{-1}) lies below both TSs [6]. This does not appear to be the case (see Fig. 1) and instead we propose that (limited) H/D exchanges prior to the loss of water, take place *after* the rate-determining TS 2 has been surmounted. The ions $^{\bullet}CH_2-O^+(CH_3)-D\cdots OD_2$ (**5**) formed from the starting ion $^{\bullet}CH_2-O(D)\cdots D-O(D)-CH_3^+$, may undergo proton-transport catalysis to produce $CH_3-O-CH_2-D^{\bullet+}\cdots OD_2$ (**6**) via TS 5. In this reaction, the D_2O picks up the oxygen bonded D and transports it to the $CH_2^{\bullet}$ group. This D can then be transported back, but this will not lead to H/D exchange. However, in a Quid pro Quo [4r,9] mechanism (TS also at 118.8 kcal mol^{-1}) the D_2O in $CH_3-O-CH_2-D^{\bullet+}\cdots OD_2$ picks up the D and then donates one of its own D's to the incipient $CH_3-O-CH_2^{\bullet}$ radical to produce $CH_3-O-CH_2D^{\bullet+}\cdots OD_2$. In a reverse reaction, the D_2O can now abstract a H^+ and donate a D^+ to the oxygen atom thereby producing ions $^{\bullet}CHD-O^+(CH_3)-D\cdots OHD$ which can lose HDO. Repeating this process would eventually also lead to loss of H_2O. In the statistical limit, the losses of H_2O:HDO:D_2O would be 10:60:30. The observed losses are 1:43:56 [6] and this indicates that the H/D exchanges are far from complete. This is not surprising as these exchanges take place after the rate-determining step has been surmounted and so they will be incomplete. In ion **6**, the water molecule could migrate to the other methyl group and this would lead to positionally equivalent methyl groups. However, loss of $CH_3^{\bullet}$ is atom specific [6] indicating that dissociation of energy rich **6** is faster than rearrangement.

A similar situation applies to the labeled starting ion $CH_3-O^{\bullet}\cdots D-O(D)-CD_3^+$, **3**, but here analysis is less straightforward because in this case a mixture of labeled ions **5** will already be present after passing TS 2, namely, $^{\bullet}CH_2-O^+(CD_3)-H\cdots OD_2$ (which loses D_2O) and $^{\bullet}CH_2-O^+(CD_3)-D\cdots OHD$ (which loses HDO). H/D exchange in $CD_3-O-CH_2D^{\bullet+}\cdots OHD$ (after PTC) would lead to loss of H_2O, but the corresponding signal will coincide with that for the loss of $CD_3^{\bullet}$.

We have also entertained the possibility that ions **3** can rearrange directly to **6** (instead of the sequence **3** → **4** → **5** → **6**) via an S_N2 type reaction via the TS $CH_3-O^{\bullet}\cdots CH_3^+\ldots OH_2$ similar to the transformation **4** → **5**. The associated TS is calculated to lie at 140.5 kcal mol^{-1} (TS8) and so this possibility can be ruled out.

Finally, we note that the bare ylid ion $^{\bullet}CH_2-O^+(H)-CH_3$ is calculated to have a higher heat of formation than its conventional isomer $CH_3-O-CH_3^{\bullet+}$, the opposite of what is found for the lower homologues $^{\bullet}CH_2OH_2^+$ and $CH_3OH^{\bullet+}$ [2,3].

3.6. *Charge transfer in ion* **2**

From labeling experiments, Tu and Holmes [6] concluded that charge exchange in ion **2** is a minor process only. Our calculations indicate that the associated charge transfer complex, i.e., TS 3, lies very close to the rate-determining step, TS 2 (see Fig. 1). Therefore, charge transfer would in principle be possible. The fact that it occurs to a minor extent only [6], indicates that electron transfer is not very probable. Further investigation of this phenomenon would appear appropriate.

*3.7. Stabilization energies of the hydrogen-bridged radical cations **3**, **4** and **5**. Comparison of CBS-QB3 with Meot-Ner's (Mautner's) correlation*

We have encountered three $OH^+\cdots O$ hydrogen-bridged radical cations on the potential energy surface, viz. **3**, **4** and **5** and their computed heats of formation (ΔH_f) are given in Table 1. For proton-bound dimers, $M_1H^+\cdots M_2$, Meot-Ner (Mautner) [15], following work by Larson and McMahon [16], found a linear correlation between the stabilization energy (SE) and the difference ΔPA between the proton affinities of M_1 and M_2 (PA $[M_1] > $ PA $[M_2]$). For $OH^+\cdots O$ bonded species the following correlation applies: $SE = (30.4–0.30\Delta PA)$ kcal mol^{-1}. Using this procedure we find the following SEs (kcal mol^{-1}) with the CBS-QB3 results in brackets: SE (**3**) = 26.2 (25.2), SE (**4**) = 25.9 (25.1) and SE (**5**) = 28.5 (26.8). It can be seen that the agreement between the correlation method and the CBS-QB3 procedure is good. (The necessary PAs were taken or calculated from the data in ref. [7], except for PA $[^{\bullet}CH_2OH] = 167$ kcal mol^{-1}, calculated from the revised value for ΔH_f $[^{\bullet}CH_2OH] = -4$ kcal mol^{-1} [8] and PA $[^{\bullet}CH_2–O–CH_3] = 173$ kcal mol^{-1} calculated from ΔH_f $[^{\bullet}CH_2–O^+(H)–CH_3] = 189.7$ kcal mol^{-1}, this work, Table 3.) These SEs are smaller than the single value (32 kcal mol^{-1}) used by Tu and Holmes [6] to estimate the heats of formation of ions **3**, **4** and **5** which are thus correspondingly lower than our calculated values.

4. Conclusions

Our calculations indicate that the proposed transformation of Tu and Holmes [6], viz. $CH_3OH^{\bullet+}/CH_3OH \rightarrow CH_2OH_2^{\bullet+}/CH_3OH$ can best be viewed as the acid-catalyzed rearrangement $CH_3O^{\bullet}/CH_3OH_2^+ \rightarrow CH_2OH^{\bullet}/CH_3OH_2^+$ where $CH_3OH_2^+$ is the acid. This rearrangement is not a 1,2-H shift taking place in the radical part of the complex (which would constitute a "spectator" process), but rather the reaction is best viewed as a Quid pro Quo [4r,9] type of catalyzed isomerization where the $CH_3OH_2^+$ ion donates a *proton* to $CH_3O^{\bullet}$ and at the same time one of the CH_3O *protons* is donated back, see TS0, Scheme 1. By contrast, the Quid pro Quo reactions observed so far involve transfer of a proton followed by transfer of a hydrogen *atom*. Thus, the neutral acetamide within the complex $CH_3C(=O)NH_2\cdots C_6H_5CN^{\bullet+}$ is transformed to its ionized enol $CH_2{=}C(OH)NH_2^{\bullet+}$ via a proton transfer from C_6H_5CN to the oxygen atom of acetamide, follwed by transfer of a CH_3 H atom back to the $C_6H_4CN^{\bullet}$ radical [4o].

The complex $^{\bullet}CH_2–O(H)\cdots H–O(H)–CH_3^+$ can isomerize via an S_N2 reaction via $^{\bullet}CH_2–O(H)\cdots CH_3^+\cdots OH_2$ into $^{\bullet}CH_2–O^+(CH_3)–H\cdots OH_2$ which represents a solvated distonic ion and which may undergo proton-transport catalysis to produce $CH_3–O–CH_2–H^{\bullet+}\cdots OH_2$.

Acknowledgements

We thank Professor John Holmes for stimulating discussions. PJAR thanks the Netherlands Organization for Scientific Research (NWO) for making available the SGI TERAS computer of SARA (Amsterdam).

References

[1] (a) B.F. Yates, W.J. Bouma, L. Radom, Tetrahedron 22 (1986) 6225;
(b) S. Hammerum, Mass Spectrom. Rev. 7 (1988) 123.
[2] W.J. Bouma, R.H. Nobes, L. Radom, J. Am. Chem. Soc. 104 (1982) 2929.
[3] (a) W.J. Bouma, J.K. MacLeod, L. Radom, J. Am. Chem. Soc. 104 (1982) 2930;
(b) J.L. Holmes, F.P. Lossing, J.K. Terlouw, P.C. Burgers, J. Am. Chem. Soc. 104 (1982) 2931.
[4] (a) D.K. Bohme, Int. J. Mass Spectrom. Ion Processes 115 (1992) 95;
(b) P. Mourgues, H.E. Audier, D. Leblanc, S. Hammerum, Org. Mass Spectrom. 28 (1993) 1098;
(c) H.E. Audier, D. Leblanc, P. Audier, T.B. McMahon, S. Hammerum, J. Chem. Soc. Chem. Commun. (1994) 2329;
(d) P.K. Chou, R.L. Smith, L.J. Chyall, H.I. Kenttämaa, J. Am. Chem. Soc. 117 (1995) 4374;
(e) J.W. Gauld, H.E. Audier, J. Fossey, L. Radonm, J. Am. Chem. Soc. 118 (1996) 6299;
(f) J.W. Gauld, L. Radom, J. Am. Chem. Soc. 119 (1997) 9831;
(g) H.E. Audier, J. Fossey, P. Mourgues, T.B. McMahon, S. Hammerum, J. Chem. Phys. 100 (1996) 18380;
(h) S.P. de Visser, L.J. de Koning, N.M.M. Nibbering, J. Am. Chem. Soc. 120 (1998) 1517;
(i) M.A. Trikoupis, J.K. Terlouw, P.C. Burgers, J. Am. Chem. Soc. 120 (1998) 12131;
(j) A.J. Chalk, J. Am. Chem. Soc. 121 (1999) 1574;
(k) M.A. Trikoupis, D.J. Lavorato, J.K. Terlouw, P.J.A. Ruttink, P.C. Burgers, Eur. Mass Spectrom. 5 (1999) 431;
(l) G. van der Rest, P. Mourgues, J. Tortajada, H.E. Audier, Int. J. Mass Spectrom. 179–180 (1998) 293;
(m) J. Chamot-Rooke, G. van der Rest, P. Mourgues, H.E. Audier, Int. J. Mass Spectrom. 195–196 (2000) 385;
(n) G. van der Rest, H. Nedev, J. Chamot-Rooke, P. Mourgues, T.B. McMahon, H.E. Audier, Int. J. Mass Spectrom. 202 (2002) 161;
(o) M.A. Trikoupis, P.C. Burgers, P.J.A. Ruttink, J.K. Terlouw, Int. J. Mass Spectrom. 210–211 (2001) 489;
(p) P. Mourgues, J. Chamot-Rooke, G. van der Rest, H. Nedev, H.E. Audier, T.B. McMahon, Int. J. Mass Spectrom. 210–211 (2001) 429;
(q) M.A. Trikoupis, P.C. Burgers, P.J.A. Ruttink, J.K. Terlouw, Int. J. Mass Spectrom. 217 (2002) 97;
(r) M. Haranczyk, P.C. Burgers, P.J.A. Ruttink, Int. J. Mass Spectrom. 220 (2002) 53;
(s) C.Y. Wong, P.J.A. Ruttink, P.C. Burgers, J.K. Terlouw, Chem. Phys. Lett. 387 (2004) 204;
(t) C.Y. Wong, P.J.A. Ruttink, P.C. Burgers, J.K. Terlouw, Chem. Phys. Lett. 390 (2004) 176.
[5] K.M. Stirk, L. Kiminkinen, H.I. Kenttämaa, Chem. Rev. 92 (1992) 1649.
[6] Y.-P. Tu, J.L. Holmes, J. Am. Chem. Soc. 122 (2000) 3695.
[7] (a) S. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988);
(b) http://webbook.nist.gov/chemistry.

[8] J.C. Traeger, B.M. Kompe, in: J.A.M. Simões, A. Greenberg, J.F. Liebman (Eds.), Energetics of Organic Free Radicals, Blackie Academic & Professional, New York, 1996 (Chapter 3).

[9] L.N. Heydorn, P.C. Burgers, P.J.A. Ruttink, J.K. Terlouw, Int. J. Mass Spectrom. 228 (2003) 759.

[10] (a) M. Dupuis, D. Spangler, J. Wendolowski, NRCC Software Catalogue 1 Program No. QG01, GAMESS (1980).;
(b) M. Guest, J. Kendrick, GAMESS User Manual, An Introductory Guide, CCP/86/1, Daresbury Laboratories, 1986.

[11] M.J. Frisch, et al., Gaussian 98, Revision A.9, Gaussian Inc., Pittsburgh PA, 1998.

[12] (a) J.A. Montgomery Jr., M.J. Frisch, J.W. Ochterski, G.A. Petersson, J. Chem. Phys. 110 (1999) 2882;
(b) J.A. Montgomery Jr., M.J. Frish, J.W. Ochterski, G.A. Petersson, J. Chem. Phys. 112 (2000) 6532.

[13] (a) J.C. Kleingeld, N.M.M. Nibbering, Org. Mass Spectrom. 17 (1982) 136;
(b) L.M. Bass, R.D. Cates, M.F. Jarrold, N.J. Kirchner, M.T. Bowers, J. Am. Chem. Soc. 105 (1983) 7024;
(c) K. Raghavachari, J. Chandrasekhar, R.C. Burnier, J. Am. Chem. Soc. 106 (1984) 3124;
(d) J.C. Sheldon, G.J. Currie, J.H. Bowie, J. Chem. Soc., Perkin Trans. 2 (1986) 941;
(e) S.T. Graul, R.R. Squires, Int. J. Mass Spectrom. Ion Processes 81 (1987) 183;
(f) G. Bouchoux, N. Choret, Rapid Commun. Mass Spectrom. 11 (1997) 1799.

[14] P.C. Burgers, J.L. Holmes, J.K. Terlouw, J. Chem. Soc. Chem. Commun. (1984) 642.

[15] M. Meot-Ner (Mautner), J. Am. Chem. Soc. 106 (1984) 1257.

[16] J.W. Larson, T.B. McMahon, J. Am. Chem. Soc. 104 (1982) 6255.