Preference for an Ion-Neutral Complex-Mediated Pathway over a Five-Membered-Ring H Shift in the Isomerization of $\text{CH}_3\text{O}^+\text{HCH}_2\text{CH}_2$ to $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^{+\cdot}$ by Ab Initio Theory

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Ab initio theory is used to explore whether the path from $\text{CH}_3\text{OH}^+\text{CH}_2\text{CH}_2$ (1) to $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^{+\cdot}$ (5) goes by way of a conventional 1,4-H shift to form $\cdot\text{CH}_2\text{OH}^+\text{CH}_2\text{CH}_3$ (2), or via the ion-neutral complex-mediated H transfer $[\text{CH}_3\text{OHCH}_2=\text{CH}_2]^{+\cdot}$ (3) $\rightarrow$ $[\text{CH}_3\text{CH}_2\cdot\text{CH}_2\text{OH}^+]$ (4). Five levels of theory all place the highest energy point in the complex-mediated reaction $3 \rightarrow 4$ slightly below that for the 1,4-H shift $1 \rightarrow 2$, but both routes appear energetically feasible near the threshold for the dissociation of 1 to $\text{CH}_3\text{CH}_2 + \text{CH}_2=\text{OH}^+$. Thus, 1 may take both paths to 5. It is concluded that when both a conventional and a complex-mediated pathway seem plausible in a given system, the latter should be considered to be as likely as the former. Ab initio descriptions of other species involved in the isomerization of 1 to 2 also are presented. (*J Am Soc Mass Spectrom* 1995, 6, 1037–1046)

It is a special privilege to contribute to this issue of the *Journal of the American Society for Mass Spectrometry* that honors Fred McLafferty. One of us (DJM) has benefited from Fred's guidance and support for nearly 30 years and from his contributions to mass spectrometry for several years longer than that. Over that period it has been inspiring to observe Fred's continuing leadership in the progress of mass spectrometry from mass 100 to beyond mass 100,000. May it continue for many years to come! It is a testimony to the breadth of his influence on mass spectrometry that among his many contributions, Fred was an author of one of the earliest papers [1] in the area of this presentation—the application of theory to the understanding of fragmentation mechanisms.

Determination of whether an ion in the gas phase reacts by a conventional mechanism or through an ion-neutral complex when either type of pathway seems plausible is a persistent and challenging issue in gas-phase ion chemistry. By a complex-mediated reaction, we mean a reaction between two partners formed by breaking a bond in an ion to the point that the partners are held together primarily by noncovalent forces. With regard to the definition of a complex,

Morton [2] said "An ion-neutral complex is one that lives long enough for one of the partners to rotate relative to the other about an axis orthogonal to the inter-fragment axis." Recent years have seen wide application of the idea that many reactions of ions in the gas phase are complex-mediated [3–7], but reservations remain. This is exemplified by the question as to whether the β -distonic ion $\text{CH}_3\text{OH}^+\text{CH}_2\text{CH}_2$ (1) isomerizes to $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^{+\cdot}$ (5) by conventional processes (Scheme I), or by way of ion-neutral complexes (Scheme II).

Conflicting opinions have been expressed as to whether 1 reaches 5 by complex-mediated processes or by conventional isomerizations. Based on the formation of CH_3OH_2^+ and CH_2OH^+ both from 1 and in ion-molecule reactions between ethene ions and methanol, the intermediacy of 3 was proposed [8]. Part of the logic for this proposal was the assumption that CH_3OH_2^+ has to be formed through 3 from 1, which implies that 3 is formed from 1 and provides circumstantial evidence that 5 also can be formed from 1 through 3.

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Nonetheless, Holmes and co-workers [9] sharply questioned these initial conclusions, and proposed the involvement of only distonic and ylid ion intermediates in the isomerization of 1 to 5. They concluded that TS(1 → 2) is at a low energy based on the observation of a similar interconversion of $C_5H_{12}O^{++}$ homologs of 1 and 2. However, according to even their own conclusions [10, 11], the isomerizations of those higher homologs are complex-mediated, which nullifies the force of their views with regard to 1 and 2.

Holmes and co-workers [9] stated that they were investigating whether complexes involved in 1 → 5 are "other than transient intermediates." In our original work we did not specify, but it was implicit that we regarded the complexes in Scheme II as being comprised of partners able to move about each other in the Morton sense [2] or, as Postma and co-workers [12] described energized $\cdot CH_2CH_2OH_2^+$, an ion closely related to 1, "...the ethene as a positive rod to which the water molecule with its dipole is attached, but can move along and about the positively charged rod."

After our initial work, we provided evidence by ab initio methods that 2 → 5 is complex-mediated, because a conventional transition state for that reaction would be considerably higher in energy than the intermediate complex [13]. In addition, Choi et al. [14] recently presented evidence that methanol-ethene ion-neutral clusters (i.e., 3) can form 1. Nonetheless, to resolve unequivocally whether 3 and 4 are significant intermediates in 1 → 5 still requires determination of

whether the transition states that form and interconvert these complexes are higher or lower in energy than the conventional transition state for 1 → 2. The present work was undertaken to provide this information, and more generally to evaluate how favorable complex-mediated pathways are relative to classical mechanisms.

Theory

Calculations were carried out by using the Gaussian 92 suite of programs [15] on a Cray YMP8/864 computer at the Center for High Performance Computing of the University of Texas. Full optimizations that involved all electrons (i.e., frozen core approximations were not used) were performed at both the UHF/6-31G(d,p) and UMP2/6-31G(d,p) levels of theory. Energies for the transition states for 1 → 2 and 3 → 4 also were calculated at the PMP3, QCISD, and QCISD(T) levels of theory by using UMP2/6-31G(d,p) geometries.

Table 1 gives current energies for complexes and transition states, together with some previously presented theoretical results. Origins of experimental heats of formation, which are included for comparison, are provided in Table 2. Results of unrestricted Hartree-Fock calculations [UHF/6-31G(d,p)] and results that include treatment of electron correlation [UMP2/6-31G(d,p)] are both given. When the energy scale is referenced to 1 as zero, about half of the theoretical results at the UHF/6-31G(d,p) and UMP/6-31G(d,p) levels agree with each other within 10 kJ mol⁻¹, but four of the remaining results differ by more than 40 kJ mol⁻¹. Where comparisons can be made (which are all for equilibrium structures), results at one level of theory agree as well as at the other with experimental values, so there is no reason to consider one level of theory more accurate than the other. However, for two of the discrepant cases, still higher levels of theory gave relative energies in good agreement with those of UMP2/6-31G(d,p) (see footnotes g and h in Table 1), which suggests that the latter energies are better than those provided by UHF theory.

All species, including the complexes, that are presented as equilibrium structures are done so based on the lack of imaginary frequencies in the vibrational analysis; all transition states had only the required one imaginary frequency. Energies provided by theory are compared to experimental 0-K heats of formation (Table 2) because ab initio procedures give 0-K values, and 0-K experimental values are the best measures of dissociation thresholds for ions in the gas phase. The published $\Delta H_f^\circ(1)$ was presented as a 298-K value, but was determined at a higher unknown temperature [9]. The extra energy present at this higher temperature would lower AE(1) from what it would be at 298-K, so $\Delta H_f^\circ(1)$ is probably too low.

Energies found for the complexes are 69–74 kJ mol⁻¹ below those for the dissociated partners—values that seem reasonable (see the following sections on each

Table 1. Ab initio energies^a of C₃H₈O⁺ ions

	ZPVE ^d	UHF/6-31G(d,p)	Energy ^b (kJ mol ⁻¹)	UMP2/6-31G(d,p)	Energy ^c (kJ mol ⁻¹)	Exp. ^e
·CH ₂ CH ₂ OH + CH ₃ (1) ^f	265	-192.814049	0	-193.414597	0	738(0)
H ₃ CH ₂ OH + CH ₂ (2) ^f	265	-192.805917	21	-193.406808	20	749(11)
TS(1 → 2) ^{f,g}	256	-192.750406	158	-193.366440	117	
[CH ₂ =CH ₂ CH ₃ OH] ^{··} (3)	257	-192.790913	53	-193.374747	97	
CH ₂ =CH ₂ [·] + CH ₃ OH	252			-193.346237	166	883(145)
TS(1 → 3)	256	-192.789471	56	-193.373751	98	
[CH ₃ CH ₂ CH ₂ =OH] ^{··} (4) ^f	256	-192.791597	50	-193.393678	46	
CH ₃ CH ₂ [·] + CH ₂ OH [·] (1)	249	-192.772684	93	-193.363210	119	848(110)
TS(3 → 4) ^h	251	-192.765221	114	-193.368192	108	
CH ₃ CH ₂ CH ₂ OH ^{··} (5) ^f	265	-192.799505	38	-193.413540	3	756(18)
[CH ₃ OH ₂ C ₂ H ₃] [·] (8)	256	-192.772447	100	-193.365462	120	
CH ₃ OH ₂ [·]	90	-115.357439 ⁱ		-115.697355		568-591
CH ₂ =CH [·]	160	-77.395901		-77.637665		257-206
CH ₃ OH ₂ [·] + C ₂ H ₃	250	-192.753340	144	-193.335020	194	825-897(87-159)
TS(3 → 8)	245	-192.757509	128	-193.360758	121	

^a Energies are for optimized structures. Structures were optimized at each level of theory starting from the optimized structure found at the previous level of theory.

^b Values obtained by combination of UHF/6-31G(d,p) energies with scaled UHF/6-31G(d,p) ZPVE.

^c Values obtained by combination of UMP2/6-31G(d,p) energies with scaled UHF/6-31G(d,p) ZPVE.

^d Values are from frequencies calculated at the UHF/6-31G(d,p) level; calculated frequencies were scaled by multiplying by a factor of 0.89.

^e Values are from Table 2.

^f Theoretical values from ref 13.

^g Values from present work at higher levels of theory: PMP3, -193.389786; QCISD, -193.399393; QCISD(T), -193.417301.

^h Values at higher levels of theory: PMP3, -193.390374; QCISD, -193.403590; QCISD(T), -193.421316.

ⁱ RHF 6-31G(d,p) calculation.

Table 2. Thermochemical data^a

Species	298 K	0 K
·CH ₂ CH ₂ O [·] + HCH ₃ (1)	712 ^b	738 ^c
CH ₃ CH ₂ O [·] + HCH ₂ (2)	724 ^b	749 ^d
CH ₂ =CH ₂ [·]	1066	1074
CH ₃ OH	-201.6	-190.7
CH ₃ CH ₂ [·]	118	130
CH ₂ =OH [·]		717.9 ^e
CH ₃ CH ₂ CH ₂ OH ^{··}	731	756
CH ₃ OH ₂ [·]	552.9 ^f -576 ^g	567.9 ^f -592 ^h
CH ₂ =CH [·]		257-306 ⁱ

^a Values from Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1, unless otherwise stated.

^b Value from ref 9.

^c Value obtained as for 2^d, except an additional 1 kJ mol⁻¹ was added because the internal energy given at 298 K by our ab initio calculations was 1 kJ mol⁻¹ higher than for 5.

^d Value obtained by adding 25 kJ mol⁻¹, ΔH_{f,0}^o(5) - ΔH_{f,298}^o(5), to ΔH_{f,298}^o(2). Our ab initio results gave the same internal energies at 298 K for 2 and 5.

^e From Ruscic, B.; Berkowitz, J. *J. Phys. Chem.* **1993**, *97*, 11451-11455.

^f From Shao, J. D.; Baer, T.; Lewis, D. K. *J. Phys. Chem.* **1988**, *92*, 5123-5128.

^g Ref 27.

^h Obtained by adding 15 kJ mol⁻¹, the difference between the values from note f, to the 298-K value in ref 27.

ⁱ Ref 26.

complex). Values provided by theory for the dissociated partners of 3 and 4 compare well with experiment, so it is likely that 3 and 4 are reasonably placed. However, QCISD(T) (quadratic configuration interaction with singles, doubles, and perturbation estimation

of triples) theory gives results in error by 32 kJ mol⁻¹ for H₂O with a bond stretched to twice its equilibrium length [16], so transition state energies are more uncertain. Unless otherwise stated, ⟨s²⟩ is less than 0.80 for each calculation, which demonstrates good quality calculations. Overlap populations, spin densities, and Mulliken charge distributions given in the following text are from the self-consistent field densities for the UMP2 (unrestricted second order Møller-Plesset perturbation) optimized structures.

In the descriptions of individual structures, overlap populations (the sums of the off-diagonal elements between atoms in the Mulliken population analysis) provide a good indication of the strength of bonding between atoms [17]; the more positive the value, the stronger the bonding. Negative values indicate antibonding interactions. Mulliken charge distributions are obtained by adding half of each overlap population to each of the two atoms it joins. This procedure is somewhat arbitrary and does not give precisely the "net" charges on the atoms in a molecule. Spin densities on atoms are obtained in a fashion similar to that for Mulliken charge distributions. A negative sign of spin density on a particular atom means that theory gives that atom a net spin opposite to that of the net spin on the ion as a whole. The spin densities we report have the same shortcomings as the Mulliken charge distributions. However, comparison of both types of values between structures does give an indication of shifts in electron distributions.

To obtain an indication of the relative rates of complex formation versus isomerization, Rice-Rams-

Figure 1. Potential energy diagram for conversion of $\text{CH}_3\text{OH}^+\text{CH}_2\text{CH}_2^+$ (1) to $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+$ (5) and related reactions. Each species is placed at an energy given in Table 1 and obtained by UMP2/6-31G(d,p) theory + ZPVE corrections. The products $\text{CH}_3\text{OH}_2^+ + \text{CH}=\text{CH}_2$ are placed at an unspecified high energy because the energy obtained for those species may not be accurate (see subsection on $[\text{CH}_3\text{OH}_2^+ \text{CH}=\text{CH}_2]$).

perger-Kassel-Marcus (RRKM) calculations were done on those reactions by using the program of Hase and Bunker [18]. Frequencies and critical energies provided by present ab initio calculations were used in these calculations.

Comparison of the Conventional and Complex-Mediated Pathways from 1 to 2 and 5

Ab initio energies for conventional ions, ion-neutral complexes and transition states are given in Table 1, and a diagram of the portion of the $\text{C}_3\text{H}_8\text{O}^+$ energy surface derived from values in Table 1 is presented in Figure 1. Optimized geometries for the species in Figure 1 are given in Figures 2-10. Starting from 1, the conventional transition state for isomerization to 2 has a five-membered-ring geometry and the complex-mediated route is $1 \rightarrow 3 \rightarrow 4 \rightarrow 2$ or 5. We will provide an overview of these two pathways from 1 to 5 in this section, with emphasis on comparison of the transition state energies for the rate-determining steps in the two pathways, that is, for $\text{TS}(1 \rightarrow 2)$ and $\text{TS}(3 \rightarrow 4)$. Individual stationary points are discussed more fully in sections that follow.

Whether $1 \rightarrow 2$ is complex-mediated or takes place by a conventional transition state is determined primarily by whether $\text{TS}(1 \rightarrow 2)$ or $\text{TS}(3 \rightarrow 4)$ is higher in energy, because $\text{TS}(3 \rightarrow 4)$ is the highest energy point in the pathway through the complexes (Figure 1). UMP2/6-31G(d,p) theory places $\text{TS}(3 \rightarrow 4)$ 9 kJ mol^{-1} below $\text{TS}(1 \rightarrow 2)$, and PMP3, QCISD, and QCISD(T) levels of theory by using the UMP2/6-31G(d,p) geometries, respectively, placed the transition state for the complex-mediated H transfer 1.5, 11, and 11 kJ mol^{-1} below the conventional transition state for $1 \rightarrow 2$. The UHF/6-31G(d,p) level of theory placed $\text{TS}(3 \rightarrow 4)$ even further (44 kJ mol^{-1}) below the con-

ventional state. Because five levels of theory place $\text{TS}(3 \rightarrow 4)$ below $\text{TS}(1 \rightarrow 2)$, according to theory, *complex-mediated isomerization of 1 to 2 is favored over the conventional pathway*. Uncertainties in the values provided by theory are large enough that this is not guaranteed to be true for this system, but the values are close enough that there must be systems in which complex-mediated isomerizations dominate conventional isomerizations. Therefore we conclude that in the absence of strong evidence to the contrary, *mechanisms that involve complexes should be considered as likely as conventional mechanisms when both types appear plausible*.

UMP2/6-31G(d,p) theory places $\text{TS}(1 \rightarrow 2)$ 2 kJ mol^{-1} below $\Delta H_f(\text{CH}_3\text{CH}_3) + \Delta H_f(\text{CH}_2=\text{OH}^+)$. Thus, $1 \rightarrow 2$ also might occur by conventional H transfer at the threshold for dissociation, so pathways I and II may operate simultaneously in the low energy reactions of 1. To improve insight into the relative rates of complex formation versus conventional isomerization, we performed RRKM calculations on the rates of $1 \rightarrow 3$ and $1 \rightarrow 2$ by using the transition state energies and frequencies derived from our UMP2/6-31G(d,p) calculations as inputs. According to these calculations, $1 \rightarrow 3$ is about 10^5 times faster than the conventional isomerization $1 \rightarrow 2$ and remains orders of magnitude faster up to above 400 kJ mol^{-1} of internal energy. However, at higher energies $1 \rightarrow 3$ would presumably become the rate of dissociation of the partners [19] rather than that for formation of 3.

A higher system homologous to 1 and 2 readily shifts a *t*-butyl group between C and O of CH_2OH [11], which suggests that 4 can access either 2 or 5. However, there appears to be a barrier to addition of methyl to the O, but not to the CH_2 of $\text{CH}_2=\text{OH}^+$ [20], so 4 may more readily go to 5 than to 2.

Definition of the Complexes and Description of Passage through Them

Present work places complex 3 in a potential minimum. There are at least three transition states that connect 3 to other structures (see following sections), and 3 also should dissociate simply. The geometries of the identified transition states vary substantially (Figures 6, 8, and 10) and are only 1-24 kJ mol^{-1} above 3 according to UMP2/6-31G(d,p) theory, so 3 is in a well that is wide and shallow. Thus slight excess energies should permit substantial movement of the partners relative to each other, in the spirit of Morton's reorientation criterion [2] for identification of a complex. Ordinarily a chemical species is considered to be differentiated from another by the transition state between them. Therefore we consider the $\text{C}_3\text{H}_8\text{O}^+$ system to be 3 as long as it is between transition states that connect it to other species. This view solves the problem of defining complexes that possess associated potential minima, but it does not define complexes that do not, for example, $[(\text{CH}_3)_2\text{CH}^+ \text{CH}_3]$ [21].

TS(3 $\rightarrow$ 8) also is placed only 1 kJ mol $^{-1}$ above 8, so the minimum for 8 is also very shallow. This is probably also the case for 4, although we did not locate TS(4 $\rightarrow$ 2) and TS(4 $\rightarrow$ 5), as would be required for verification.

Given that the intermediate complexes are in wide shallow wells, the system probably goes from 1 to 2 and/or 5 through 3 and 4 as we have defined them, but not usually right through the associated energy minimum. We previously concluded that the methyl radical-propyl ion pair (which does not have a minimum) from the *n*-butane ion eliminates methane while skirting an accessible minima [21].

Structures and Energies of Pertinent Species

$\text{CH}_3\text{OH}^+ \text{CH}_2\text{CH}_2$ (1)

The structure found for 1 by theory is depicted in Figure 2. It is at the low point on the region of the $\text{C}_3\text{H}_8\text{O}^{+}$ potential energy surface that we explored. This ion has a nearly trans orientation about the inner C—O bond, a bond which is longer (1.55 Å) than the other C—O bond (1.49 Å). The C—C bond in 1 is shortened with respect to the normal single C—C bond length (1.46 Å compared to 1.53 Å in C_2H_6) at a similar level of theory [MP2/6-31G(d)]. The terminal CH_2 is rotated by about 15° from where its singly occupied p orbital eclipses the oxygen. The overlap population for the terminal C—O bond is 0.21, and that for the central C—O bond is 0.12; the latter value together with the slight elongation of the central C—O bond suggests some loosening of that bond, although in its ground state 1 is clearly a conventional structure rather than a complex.

The spin is almost exclusively on the terminal CH_2 (spin density = 1.18) in 1. The Mulliken charges are +0.54 on the methyl, −0.15 on the OH, +0.46 on the internal CH_2 and +0.15 on the terminal CH_2 . All of the hydrogens have Mulliken charges of about +0.2, except that for the protonating H on oxygen which is +0.44.

$\text{CH}_2\text{OH}^+ \text{CH}_2\text{CH}_3$ (2)

The optimized geometry of the distonic ion 2 is displayed in Figure 3. Like 1, 2 adopts a conformation

Figure 2. UMP2/6-31G(d,p) geometry for $\text{CH}_3\text{OH}^+ \text{CH}_2\text{CH}_2$ (1).

Figure 3. UMP2/6-31G(d,p) geometry for $\text{CH}_2\text{OH}^+ \text{CH}_2\text{CH}_3$ (2).

that is almost fully extended. The dihedral angle that the C—C bond forms with the plane that contains the two C—O bonds is 178°, that is, the methyl and the terminal methylene are almost perfectly trans to each other. Also, as with 1, the central C—O bond is a little longer than the terminal bond: 1.53 Å versus 1.44 Å. The C—O bonds in 2 are slightly shorter than the corresponding bonds in 1, and the C—C bond at 1.50 Å is a little longer than the C—C bond in 1. The O—H bond is 0.98 Å long. The terminal CH_2 is slightly pyramidalized; the bond angles about it total 348°; corresponding values are 328° for a tetrahedral structure and 360° for a planar structure.

The central C—O bond has an overlap population of 0.12, as compared to 0.22 for the terminal C—O bond, values similar to those for 1. The overlap population of the O—H bond is 0.61. Similarly to 1, the Mulliken charges are +0.49 for the terminal CH_2 , −0.11 for the oxygen, +0.47 for the central CH_2 , +0.15 for the methyl, and +0.45 for the H on oxygen.

TS(1 $\rightarrow$ 2)

The transition state for the conventional isomerization of 1 to 2 is pictured in Figure 4. In the following discussion carbon atoms are referred to by numbers assigned as follows

Figure 4. UMP2/6-31G(d,p) geometry for the transition state for 1 $\rightarrow$ 2.

and the hydrogen transferred is designated H_t . This transition state has the following bond lengths to H_t : $C1H_t = 1.38 \text{ \AA}$ and $C3H_t = 1.28 \text{ \AA}$, somewhat longer than other C—H bonds in this structure, which are $1.079\text{--}1.085 \text{ \AA}$ in length. The C—C bond is $1.49 \text{ \AA}$ long. The C—O bond lengths differ somewhat: $1.47 \text{ \AA}$ to C1 and $1.55 \text{ \AA}$ to C2, but they are still close to the lengths they have in **1** and **2**. The CHC bond angle about H_t is 135° . This large angle is balanced by unusually small bond angles in the ring about C1 (90°) and C3 (97°). The large angle is probably a compromise between the preferred angle for such H atom abstractions, which is near 180° when there is no ring constraint, and the requirement that angles in the five-membered ring transition state have to average 108° in a planar structure (less in a nonplanar structure). The five-membered ring is not quite planar: C2 is 11° below the plane formed by C3, H_t , and C1 whereas the O is 20° above the plane formed by C2, C3, and H_t .

The overlap populations of H_t with C1 and C3 are 0.31 and 0.48, compared to averages of 0.79 and 0.80, respectively, for the hydrogens that remain bonded to each of these carbons. Thus in the transition state, one C—H bond breaks and a new one is formed; the transfer is slightly more than half completed. The Mulliken charge on H_t is the smallest on any H in the molecule, +0.16. For the other carbon-bound hydrogens, the Mulliken charges vary from +0.22 to +0.24, and it is +0.45 for the H on O. The carbon atoms involved with making and breaking C—H bonds have Mulliken charges of -0.036 for C1 and -0.39 for C3. The Mulliken charge on C2 is +0.051, and that on O is -0.58 .

All atoms except C1 (0.78), C3 (0.65), and H_t (-0.22) have absolute spin densities below 0.05. The spin distribution on the atoms involved in the H transfer can be viewed as representative of an electron on H_t with its spin distribution being somewhat separated from that of interacting electrons on C1 and C3. However, this suggestion is subject to the reservation that the method to determine spin distributions is quantitatively uncertain.

$[CH_3OH \cdot CH_2=CH_2]^+ \cdot (3)$

The geometry obtained for the complex **3** is presented in Figure 5. This complex was placed in a potential minimum by UMP2/6-31G(d,p) theory because it had no imaginary vibrational frequencies. The theoretical energies of **3** and TS(**1** $\rightarrow$ **3**) differ by only 1 kJ mol^{-1} , which demonstrates that substantial changes in geometry are associated with very small changes in energy. Thus, as previously stated, the partners in **3** are probably fairly free to move about each other.

$C_2H_4^+$ is planar at the UMP2/6-31G(d,p) in our calculations, both in **3** and in isolation. However, Bellville and Bauld [22] found $C_2H_4^+$ to be nonplanar by theory, as have good experiments [23]. The oxygen in optimized **3** is in the plane of the C_2H_4 and equidis-

Figure 5. UMP2/6-31G(d,p) geometry for $[CH_3OH \cdot CH_2CH_2]^+ (3)$.

tant from both the ethene carbons ($2.94 \text{ \AA}$) and the closest ethene hydrogens ($2.24 \text{ \AA}$). These C—H distances are the smallest of any interatomic distances between the two partners. The methyl group projects out of the ethene-oxygen plane and is also equidistant between equivalent atoms in the $C_2H_4^+$ moiety. The C—O distances to the ethene carbons are almost twice the length of the C—O bonds in **1**. The C—H bonds in $C_2H_4^+$ that are toward the oxygen are perhaps slightly longer ($0.001 \text{ \AA}$) than the C—H bonds that point away from the oxygen. Bond angles are more distorted; the H—C—C bond angles in the $C_2H_4^+$ portion are 118° for the hydrogens toward the oxygen versus 122° for the opposite hydrogens. The C—C bond length in **3** is $1.41 \text{ \AA}$, and the associated overlap population is 0.78. These are essentially identical at the same level of theory within the accuracy of the calculation (with standard cutoffs) as for isolated $C_2H_4^+$: $1.41 \text{ \AA}$ and a corresponding overlap population of 0.77. The CH_3OH in **3** has a geometry very close to that of CH_3OH : the C—O lengths are $1.44 \text{ \AA}$ (in **3**) and $1.42 \text{ \AA}$ (in CH_3OH), and O—H lengths are 0.96 in both **3** and CH_3OH .

The overlap populations between the oxygen and the nearest hydrogens of the $C_2H_4^+$ are both 0.037, much smaller than the 0.62 for the hydrogen bonded to the oxygen. The overlap populations for the C—H bonds in the $C_2H_4^+$ are 0.75 for the proximal pair and 0.77 for the distal pair. Thus there is little covalent interaction between the partners in **3**. In **3** the Mulliken charge distribution places 96% of the charge on the C_2H_4 part, and the spin on the C_2H_4 atoms totals 1.00. In summary, **3** is well described as a methanol-ethene ion complex.

In earlier work **3** was estimated to be 70 kJ mol^{-1} lower in energy than its dissociated partners [8] based on a theoretical noncovalent binding energy of 70 kJ mol^{-1} between $C_2H_4^+$ and H_2O [12]. The binding energy for **3** at the UMP2/6-31G(d,p) level is 69 kJ mol^{-1} , which suggests that such extrapolations can be confidently made for ion-dipole complexes without the need for elaborate computations. Experiment places the binding energy in **3** in excess of 33 kJ mol^{-1} [24], at least consistent with theory. However, results for **4** (see following text) imply that such extrapolations do

not work as well when the species under consideration differs significantly from the reference species—differences that may be revealed only by theory.

TS(1 → 3)

The transition state for the dissociation of 1 to the complex 3 is shown in Figure 6. This transition state is similar in structure to 3, but much less symmetrical. The C_2H_4^+ moiety is nonplanar with the CH_2 groups twisted by about 15° with respect to each other. The oxygen already is remote from both ethene carbons (2.79 and 2.86 Å), although not quite as far away as in 3. The C—C bond length in this transition state (1.41 Å) is already the same length as it is in 3 (1.41 Å). The oxygen is 37° out of the plane of the closer CH_2 of the C_2H_4^+ . (This angle was used as the principal variable in the search for this transition state.) The methylene group that contains the other carbon has the hydrogen nearer oxygen tilted toward the oxygen, as though to maintain weak bonding between these atoms.

The overlap population between the oxygen and incipient ethene carbons is negative in this transition state, as it is in the complex, which demonstrates that the bond between the partners is already fully broken. The overlap populations between the oxygen and the two hydrogens nearest to it on C_2H_4^+ are positive; they average 0.023, 38% lower than in 3.

$[\text{CH}_3\text{CH}_2^+ + \text{HO}=\text{CH}_2]$ (4)

The complex 4 is drawn in Figure 7. Our vibrational analysis places 4 in a potential energy minimum, but we have no estimate of its depth because we did not determine energies for TS(4 → 2) and TS(4 → 5). All of the atoms in the CH_2OH partner and the carbon atoms of the ethyl group are almost in a plane. The shortest distance between C_2H_5 and CH_2OH^+ is between the CH_2 carbon of the C_2H_5 and the hydrogen on oxygen of the CH_2OH^+ (1.66 Å). Thus the ethyl has moved from the O to the adjacent H. The CHO bond angle is almost linear (177°) and the CH_2 of the CH_2OH and the methyl are very nearly trans to each other. The

Figure 6. UMP2/6-31G(d,p) geometry for the transition state for 1 → 3.

Figure 7. UMP2/6-31G(d,p) geometry for $[\text{CH}_3\text{CH}_2^+ + \text{CH}_2=\text{OH}]^+$ (4).

O—H bond is stretched to 1.06 Å (relative to 0.98 Å in 2 and 0.98 Å in $\text{CH}_2=\text{OH}^+$). The overlap population between the CH_2 of the ethyl and the hydrogen on oxygen is 0.27, much smaller than the 0.77 average of the two hydrogens bonded to the ethyl methylene, but not too much less than the 0.33 for the formal O—H bond. Thus the $\text{CH}_3\text{CH}_2 \cdots \text{H}$ bond in 4 is almost as strong as the $\text{CH}_2\text{O} \cdots \text{H}$ bond. The O—H bond is substantially weakened as well as stretched, because its overlap population is not much more than half those in O—H in 2 and in $\text{CH}_2=\text{OH}^+$ (0.60).

Most (86%) of the Mulliken charge resides on the CH_2OH group, and 77% of the spin is on the C_2H_5 . The spin density on the radical site carbon is 0.96. (The spin density on C_2H_5 is less than it is on the radical site carbon because there were negative spin densities on other atoms in the ethyl.) The H on O bears a fairly significant spin density of +0.096. The lack of strict confinement of the charge and spin to their respective molecular parts and the stronger than expected overlap population between the CH_2 of the ethyl and the hydrogen on O makes the minimum for this complex a somewhat covalently bound species with a divalent hydrogen.

A binding energy of 20 kJ mol^{-1} was previously assumed for 4 [8] based on the binding energy between the partners in the acetyl ion-methyl radical complex [25], in contrast to the 73 kJ mol^{-1} found for 4 at the UMP/6-31G(d,p) level of theory in the present study. The larger than previously estimated binding energy in 4 may be due to the unusually strong "hydrogen bond" found in this species, a phenomenon not taken into account when the estimate was made. An experimental binding energy of $> 59 \text{ kJ mol}^{-1}$ for $[(\text{CH}_3)_2\text{CHCH}_2\text{OH}]^+$ [24] is consistent with the value from theory for 4.

TS(3 → 4)

The transition state that interconverts complexes 3 and 4 is represented in Figure 8. As in TS(1 → 2), the

Figure 8. UMP2/6-31G(d,p) geometry for the transition state for 3 → 4.

itinerant hydrogen in this transition state will be referred to as H_t . The bond length to H_t from the methanol carbon is 1.29 Å, whereas it is 1.68 Å from H_t to the closer of the two carbons in the C_2H_4 portion. The other ethene carbon is only a little further away at 1.82 Å. The overlap populations in these bonds are 0.31 to the methanol carbon and 0.051 and 0.002 to the two carbons of the C_2H_4 . This compares to averages of 0.82, 0.81, and 0.81 for the hydrogens statically bound to these carbons. Surprisingly, the C—C bond length (1.36 Å) in this transition state is shorter than in $C_2H_4^+$ (1.41 Å). The C—O bond length at 1.33 Å is intermediate between the 1.25 Å of 4 and the 1.44 Å of 3. The transition state is more like methanol plus ionized ethene than it is like ethyl and protonated formaldehyde, at least insofar as the bond lengths to H_t and the associated overlap populations are concerned.

The $OC1H_t$ bond angle is a near normal 108°, and the angle about H_t is 155°. The bond angle about the ethylenic carbon about to receive H_t (CCH_t) is 73°. This is intermediate between the CCH angles for $C_2H_5^+$ (59°) and C_2H_5 (112°) [C. E. Hudson, unpublished UHF/6-31G(d,p) observations].

The Mulliken charge distribution mirrors the early nature of the transition state. The C_2 portion retains 63% of the positive charge, whereas the CH_2OH bears 36%. The charge on H_t , +0.01, is the smallest on any hydrogen in this transition state. The charges on the other hydrogens vary from +0.20 to +0.40 and average +0.26.

Although 3 → 4 is a hydride transfer, there are ways in which its transition state strongly resembles the transition state (TS) for a hydrogen atom transfer. The nearly equal distance between the two carbons of the C_2H_4 portion and H_t suggests that the C_2 portion of the TS is positioned to receive H_t as an atom headed toward bridged $C_2H_5^+$. One would expect for a pure hydride ion transfer that the spin, which starts and ends on the C_2 portion, would remain there in the

TS. However this is not the case at all. The spin densities on CH_2OH in TS(3 → 4) total 0.53, and they total 0.54 on the C_2H_4 portion. This resembles the distributed spin densities noted previously on the two carbons involved in the H atom transfer in TS(1 → 2). The spin density on H_t is −0.068. This has the same sign as the spin density in the hydrogen atom transfer reaction 1 → 2, although the spin density in the latter reaction on the hydrogen transferred in 1 → 2 is three times as large as on H_t in the present case. The spin density on H_t may be less than that for a typical hydrogen atom transfer reaction, but it is still (in absolute value) more than twice as large as that of any other hydrogen in this transition state. (Those spin densities vary from −0.031 to +0.0005.) In short, TS(3 → 4) has some of the character of both hydride and hydrogen atom transfers. This transition state apparently serves to get the hydrogen transferred, with the final charge distribution established later.

$[CH_3OH_2^+ CH_2=CH^{\cdot}]$ (8)

The complex 8 is presented in Figure 9. At its minimum energy, 8 is a "hydrogen-bonded" species like 4. The closest approach of the partners is the 1.89 Å between the radical site carbon and one of the hydrogens on oxygen. The distance from that hydrogen to the other vinyl carbon is 2.02 Å. Thus the bridging hydrogen is directed toward the π bond in the vinyl group. The O—H bond lengths are 0.97 and 1.03 Å; the hydrogen closer to the vinyl has the longer bond. The bond angle about the hydrogen that bridges the two fragments is a nearly linear 163°. The overlap populations for the O—H bonds are 0.61 and 0.40; the atom closest to the vinyl radical is less strongly bound. The overlap population between the bridging H and the associated carbon is 0.17, much less than the 0.77 for the C—H bond of the radical site carbon. The spin density on the bridging hydrogen is small (−0.005). The protonated methanol portion of 8 has 85% of the positive charge, whereas the vinyl radical portion has atomic spin densities that total 1.00 electrons. The spin density on the radical site carbon is 1.45 and that on the other vinyl carbon is −0.58. The spin densities are similarly split in the vinyl radical: −0.73 on the methylene and +1.60 on the other C.

Figure 9. UMP2/6-31G(d,p) geometry for $[CH_3OH_2^+ CH_2=CH^{\cdot}]$ (8).

The UMP2/6-31G(d,p) energy for $\text{CH}_3\text{OH}_2^+ + \text{CH}_2=\text{CH}^\cdot$ is 45–107 kJ mol^{-1} above the range of experimental values, our largest difference. $\langle s^2 \rangle = 0.87$ for this complex is substantially higher than 0.75, the ideal value for an uncontaminated doublet, $\langle s^2 \rangle$ for the vinyl radical is unusually large in most calculations:

1.01 at the UHF/6-31G(d,p) optimum structure.

0.93 at the MP2/6-31G(d,p) optimum.

0.96 at the UHF/6-311 + G (2df,p) optimum.

Annihilation of the first spin contaminant improved $\langle s^2 \rangle$ to 0.755 (PMP2 level of theory), but only reduced the energy difference between CH_3OH_2^+ and $\text{CH}_2=\text{CH}^\cdot$ and 1 to 173 kJ mol^{-1} from 194 kJ mol^{-1} at the UMP2/6-31G(d,p) level. Reduction of spin contamination brings the difference between theoretical results and the upper limit for the experimental energies to 14 kJ mol^{-1} , and favors the higher experimental values. A wide range of experimental energies exists for the vinyl radical [26], which makes evaluation of the results from theory uncertain. Higher levels of theory [26] agree reasonably with experiment for the vinyl radical. Treatment of CH_3OH_2^+ at a level of theory similar to the higher level applied here also gives a result in good agreement with experiment [27].

TS(3 $\rightarrow$ 8)

The transition state for the proton transfer from C_2H_4^+ to CH_3OH in 3 $\rightarrow$ 8 is depicted in Figure 10. This transition state has the migrating hydrogen 1.32 Å from the carbon it departs and 1.23 Å from the oxygen it joins. The overlap populations to this hydrogen are 0.52 and 0.15, respectively, compared to values of 0.75 and 0.61 for the hydrogens fully bonded to the respective atoms. The C=C bond length of 1.33 Å is closer to that of the vinyl radical (1.29 Å) than to that of C_2H_4^+ (1.41 Å).

The spin remains on the hydrocarbon portion throughout the transfer. The spin density on the CH_3OH totals 0.014 electrons. The spin density on the hydrogen that is transferred has the largest absolute value of that on any hydrogen in the molecule at -0.020 . If half of this value is considered to belong to

each partner, then the C_2H_3 has 99.6% of the spin in the TS. Despite the fact that the C—C bond length is near that of a full double bond as in the vinyl radical, the spin density is not strongly localized on the CH carbon atom. The spin densities are 0.53 for that carbon and 0.48 at the adjacent carbon. This distribution is much more like that of the ethene ion than that of the vinyl radical (see preceding section).

The Mulliken charge on the hydrogen atom that is transferred is +0.45, which is the largest on any hydrogen in this TS. The other hydrogens on the C_2H_3 average +0.25, the methyl hydrogens average +0.18, and the methanol O—H averages +0.40. The charge concentration on the migrating hydrogen in TS(3 $\rightarrow$ 8) is appropriate for this proton transfer. The carbons and oxygen all have negative Mulliken charges. If the charge on the atom that is transferred is considered equally distributed between the C_2H_3 and CH_3OH portions, then the former bears 59% of the charge and the latter 41%.

$\langle s^2 \rangle$ at the MP2 transition state is 0.79, which suggests that the characteristics found for this transition state are reasonable.

TS for Direct Formation of CH_3OH_2^+

An effort was made to locate a transition state for concerted α - β elimination of CH_3OH_2^+ from 1. As the O and appropriate H were forced together beyond ring angles of 90°, the C—O and C—C bond within the ring lengthened substantially, and the affected C—H bond compressed. The forces to drive the system back toward 1 were very large at this point, which illustrates once again that concerted α - β eliminations tend energetically to be highly unfavored processes [28]. The high energy for direct formation of CH_3OH_2^+ demonstrated by present calculations clearly verifies the conclusion in earlier experimental work [8] that formation of CH_3OH_2^+ from 1 is complex-mediated.

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Figure 10. UMP2/6-31G(d,p) geometry for the transition state for 3 $\rightarrow$ 8.

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