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Dissociation of Ionized 1,2-Ethanediol and 1,2-Propanediol: Proton-Transport Catalysis with Electron Transfer[†]

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Ab initio molecular orbital (MO) calculations support the proposal that the key processes in the rearrangement of $HOCH_2CH_2OH^{\bullet+}$ and $HOCH_2CH(CH_3)OH^{\bullet+}$ (ionized 1,2-ethanediol and 1,2-propanediol) are sequential transfers of a *proton* and an *electron* taking place from one partner to the other in ion−dipole complexes rather than prompt hydrogen *atom* shifts taking place in distonic ions. Although the proposed distonic ions in the alternative mechanism (*J. Am. Chem. Soc.* **1992**, *114*, 2027) are thermodynamically remarkably stable species, a surprisingly large barrier exists for their interconversion by way of a 1,4-H *atom* shift. This large barrier results from significant distortion, from planarity, of the transition state. The rearrangement process of ionized 1,2-ethanediol and 1,2-propanediol can therefore best be described in terms of intramolecular catalysis (proton transport catalysis, *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 95) in combination with an electron transfer taking place in intermediate ion−dipole complexes.

Introduction

The unimolecular chemistry of low-energy 1,2-ethanediol radical cations, **1**, is very interesting for a number of reasons.[1] It is one of those cases where the time-honored technique of isotopic labeling led to completely unexpected results. The radical cation $HOCH_2CH_2OH^{\bullet+}$, **1**, is but one of many that dissociate via a so-called double hydrogen transfer (DHT), and for **1** this reaction produces $CH_3OH_2^+$, *m/z* 33, + $HCO^\bullet$.[1] Over the past decade no less than four mechanisms have been proposed for this reaction. Ten years ago, we proposed[2] that the reaction proceeded via a 1,5-hydrogen shift (**4** → **7**) in the hydrogen-bridged intermediate **4**:

$$\mathbf{1} \rightarrow CH_2{=}O\cdots H^+\cdots O(H){-}CH_2^\bullet\ (\mathbf{4}) \rightarrow HC^\bullet{=}O\cdots H^+\cdots O(H){-}CH_3\ (\mathbf{7}) \rightarrow CH_3OH_2^+ + HCO^\bullet$$

This followed an earlier elegant proposal by Morton[3] that hydrogen bonding in the neutral may persist upon ionization and that such bonding may account for otherwise problematic reactions. Indeed, ab initio calculations indicated that species **4** and **7** enjoy considerable stabilization and that they therefore are attractive intermediates.[2] However, at that time the transition state **4** → **7** and its energy could not be evaluated because of computational limitations. A concurrent study by Radom et al.[4] led to an alternative mechanistic proposal i.e., a 1,2-H shift in the distonic isomer[5] (**2**):

$$\mathbf{1} \rightarrow {}^\bullet OCH_2CH_2OH_2^+\ (\mathbf{2}) \rightarrow CH_3OH_2^+ + HCO^\bullet$$

The surprisingly stable ion **2** was calculated to be generated upon ionization of 1,2-ethanediol by a barrier-free 1,4-H shift.

These mechanistic proposals both prescribe that the $\mathbf{1}-(OD)_2$ labeled ion undergoes a specific loss of $HCO^\bullet$ to yield the protonated methanol isotopomer $CH_3OD_2^+$ at *m/z* 35. The specific formation of *m/z* 35 had been observed in the initial study,[2] but later MS/MS experiments[6,7] revealed that the *m/z* 35 ions had the connectivity CH_2DOHD^+ rather than $CH_3OD_2^+$ and this proved the above proposals to be incorrect. From the ab initio calculations,[2] it followed that **4** can best be viewed as a hydrogen-bridged ion−dipole complex of the methyleneoxonium ion and neutral formaldehyde, $CH_2{=}O\cdots H{-}O^+(H)CH_2^\bullet$, i.e., with the bridging hydrogen closer to the moiety of higher proton affinity. This would imply that the transition state **4** → **7** may lie prohibitively high because in order to transport one of the formaldehyde H atoms in **4** to the methylene radical site of $CH_2OH_2^{\bullet+}$, the formaldehyde molecule would have to rotate to such a degree that the resulting ion−dipole repulsion would lead to separation of the partners rather than to hydrogen transport. Nevertheless, we felt that because of their considerable stability,[2] hydrogen-bridged intermediates would still be viable mediators. Indeed, using ab initio calculations, we were able to trace a circuitous but energetically attractive route for hydrogen transfer[1] that satisfies the labeling results (see Scheme 1 and Figure 1).

First, upon ionization of ethanediol, the resulting radical cation collapses to a species, **3**, containing a long (∼2 Å), one-electron

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[†] Dedicated to Dr W. Heerma in appreciation of his contributions to mass spectrometry and his inspiring educational guidance.

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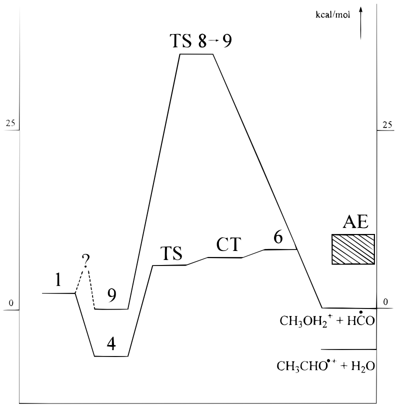
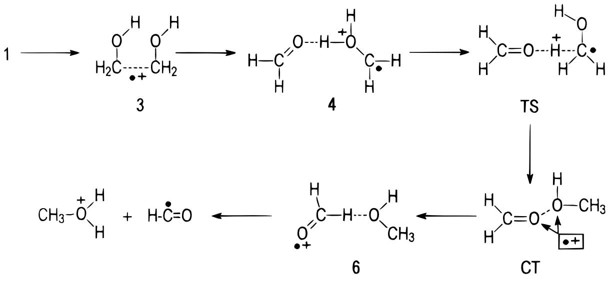
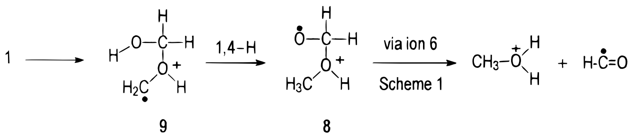


Figure 1. Theoretical results for the relative energies of isomers and transition states encountered in the dissociation of 1,2-ethanediol radical cations according to Schemes 1 and 2.

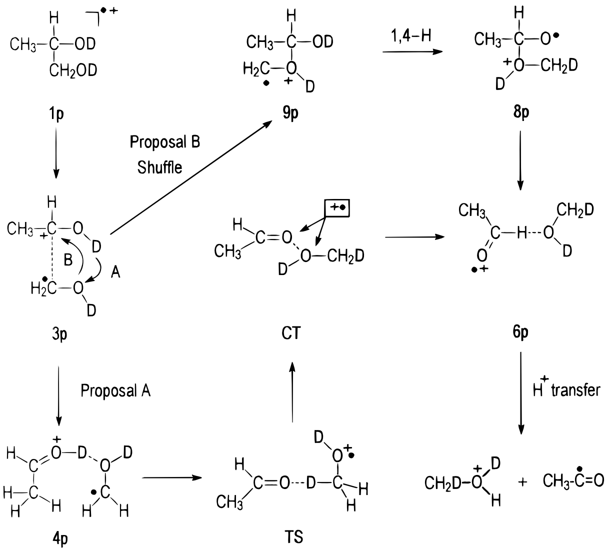
SCHEME 1



SCHEME 2



SCHEME 3



C−C bond. Further elongation of this bond leads to the H-bridged radical cation **4**. In representing ion **4** as $CH_2{=}O\cdots M^{\bullet+}$, the key questions is the following: how can we achieve hydrogen transfer to produce $HCO^{\bullet} + MH^{+}$? As stated above, rotation of the formaldehyde unit within the electrostatic field of $M^{\bullet+}$ would lead to ion−dipole repulsion ($O{=}CH_2\cdots M^{\bullet+}$) and so hydrogen transfer is not possible via this route. However, in an ion−dipole complex of the type $CH_2{=}O^{\bullet+}\cdots M$, where the formaldehyde moiety is now charged, the $CH_2{=}O^{\bullet+}$ unit can more or less freely rotate without too much loss of ion−dipole stabilization. This would produce $O{=}CH_2^{\bullet+}\cdots M$ (ion **6** in Scheme 1), which could then undergo **proton** transfer to produce $HCO^{\bullet} + MH^{+}$. Hence, hydrogen (proton) transfer in $CH_2{=}O^{\bullet+}\cdots M$ is possible only if the charge is first transferred to $CH_2{=}O$, but this is not possible for ion **4** because neutral CH_2OH_2, if it exists, is a very high-energy species. We therefore proposed, and this was substantiated by ab initio calculations, that the $CH_2OH_2^{\bullet+}$ ions first rearrange to $CH_3OH^{\bullet+}$ by a formaldehyde-catalyzed 1,2-proton shift (**4** → TS). This process is an example of Böhme's concept of "proton-transport catalysis".[8,9] It has recently been shown,[10] from chemical ionization experiments, that the reverse isomerization $CH_3OH^{\bullet+} \rightarrow CH_2OH_2^{\bullet+}$, which does not occur unassisted, is greatly accelerated by the addition of water. This has also been established by ab initio calculations.[11] The result of this "proton-transport catalysis" for ion **4** is that an ion−dipole complex is produced for which both partners ($CH_2{=}O$ and CH_3OH) represent stable neutral and ionic structures, and so now charge transfer (CT) is possible via orbital interaction.[1] Once the formaldehyde moiety becomes charged, it can rotate such that one of its hydrogen atoms becomes correctly oriented for transfer (**6**), and this transfer then is a **proton** transfer. With regard to the transformation **4** → TS, it is of interest to note that the proton affinity (PA) of $CH_2{=}O$ (PA = 168 kcal/mol) lies between that of $CH_2OH^{\bullet}$ at oxygen (to produce $CH_2OH_2^{\bullet+}$), PA = 160 kcal/mol, and that of $CH_2OH^{\bullet}$ at carbon (to produce $CH_3OH^{\bullet+}$), PA = 170 kcal/mol,[9] and so the proton transport catalysis **4** → **TS** is energetically possible as substantiated by our ab initio calculations.

Shortly before these results were reported, Audier et al.[7] reported a detailed study of the unimolecular chemistry of the methyl ether of **1**, $CH_3OCH_2CH_2OH$, which also dissociates via DHT to produce $CH_3O(H)CH_3^{+} + HCO^{\bullet}$. On the basis of labeling results and observations from ion−molecule reactions, they proposed a mechanism involving distonic ions and suggested that **1** would dissociate similarly (see Scheme 2), but no theoretical calculations were available for this process. Ion **9** could be formed from **3** via a shuffle of the two CH_2OH subunits. Both mechanisms, i.e., dissociation via either ion−dipole complexes (Scheme 1) or distonic ions (Scheme 2), are experimentally indistinguishable; for example, they both correctly predict the labeling results (see above). Note that we had already calculated[1] that if ions **8** can be formed from **1**, they could lose $HCO^{\bullet}$ via a low-lying isomerization to **6**. The question is therefore the following: can ions **8** be formed from **9** via a 1,4-hydrogen shift according to Scheme 2 at or below the experimentally determined appearance energy (AE)?

The next-higher homologue of **1**, ionized 1,2-propanediol, $HOCH_2CH(CH_3)OH^{\bullet+}$ (**1p**), also dissociates by DHT, yielding $CH_3OH_2^{+} + CH_3CO^{\bullet}$.[12] This process appears to be remarkably similar to that for **1**; for example, the isotopomer $CH_3CH(OD)CH_2OD^{\bullet+}$ specifically forms CH_2DOHD^{+} to the exclusion of $CH_3OD_2^{+}$.[12] Again, two mechanisms, one involving ion−dipole complexes (proposal A), the other distonic ions (proposal B), and which are very similar to those proposed for 1,2-ethanediol, may account for all observations (see Scheme 3). Again, the question is the following: which mechanism can occur at or below the AE ? To decide between the two mechanistic proposals for **1** and **1p**, we have performed ab initio MO calculations on the most relevant parts of the respective potential energy surfaces.

TABLE 1: Electronic Energies of Ionized 1,2-Ethanediol, ZPVE, and Relative Energies of Isomers and Transition States for This System

structure	RHF/DZP (hartree)	ZPVE[a] (kcal/mol)	SDCI/Pople (hartree)	E_{rel} [b] (kcal/mol)	E_{rel} [c] (kcal/mol)
1	−228.662 84	50.9	−229.311 74	1.9	
4	−228.672 66	47.8	−229.321 13	−6.9	
TS	−228.623 24	45.2	−229.295 84	6.2	≤9 ± 2
CT	−228.652 90	48.0	−229.299 94	6.4	≤9 ± 2
6	−228.650 27	47.8	−229.298 73	7.2	≤9 ± 2
9	−228.666 20	50.7	−229.314 85	−0.2 [−1.8][d]	
8	−228.675 60	51.4	−229.316 53	−0.5 [−1.9][d]	
TS **8** → **9**	−228.577 75	48.3	−229.254 28	35.4 [34.7][d]	≤9 ± 2
$HCO^{\bullet} + CH_3OH_2^+$	−228.651 74	47.3	−229.308 87	0	

[a] RHF/DZP scaled by 0.9 for the geometries of the ions (except for TS **8** → **9**); see ref 1. [b] Energies including ZPVE. [c] Experimental appearance energy (ref 1). [d] QCISD/6-31G**//MP2(FC)/6-31G** result (see text).

Results and Discussion

1,2-Ethanediol. Building upon the results described in ref 1 and using the same computational procedures, we have located, at the RHF/DZP level of theory, the minima for the distonic structures **8** and **9** as well as the transition state (saddle point with one imaginary frequency) connecting these ions. Electron correlation effects were then introduced by performing single + double excitation CI (SDCI) calculations including the Pople size-correction method.[13a] All minima and saddle points were checked for the correct number of imaginary frequencies, and transition states were checked for connections to appropriate minima. Note further that CT does not correspond to a minimum but to a minimum energy crossing point (see ref 1 for details). The results are given in Figure 1 and in Table 1, which include the highest barriers associated with the ion−dipole mechanism,[1] CT and **6** in Scheme 1. All energies are relative to the products, which are set to zero. We find that the barrier for the 1,4-H shift **9** → **8** is surprisingly large and, more importantly, that it lies 26 kcal/mol above the measured AE (see Figure 1). As stated, ions **8**, should they be formed, can isomerize to **6** at the AE after which dissociation to $CH_3OH_2^+$ + $HCO^{\bullet}$ would take effect.[1] For ions **8**, **9**, and TS **8** → **9**, we have also performed MO calculations at the QCISD/6-31G**//MP2(FC)/6-31G** level of theory[13] (see Table 1), which gives results almost identical to results of our SDCI calculations. From the results presented in Table 1 and Figure 1 we conclude that the 1,4-hydrogen shift **9** → **8** does not occur for the low-energy (metastable) ions and also that the dissociation of ionized 1,2-ethanediol may proceed via Scheme 1, i.e., via proton and electron transfers in ion−dipole complexes.

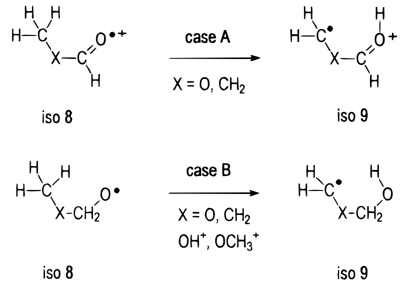
The barrier for the conversion **8** → **9** is 36 kcal/mol relative to **8**, much larger than that associated with a 1,4-H shift in other oxygen-containing cations; for example, the 1,4-H shift in ionized methyl acetate, $CH_3C({=}O)OCH_3^{\bullet+} \rightarrow CH_3C(OH)OCH_2^{\bullet+}$, requires only 12 kcal/mol.[14] A possible explanation for the increased barrier height in the present system comes from an analysis of the computational results in Table 2 on 1,4-H shifts in the ionic and neutral systems shown in Scheme 4 (case B; X = OH^+ represents ions **8** and **9** for ionized 1,2-ethanediol). In Table 2 the orientation of the singly occupied orbital, which in all cases is almost completely localized on an O atom, is indicated by σ or π. This is possible even if the structure has no overall symmetry. Here, σ indicates that the open-shell orbital lies in the XCO plane, whereas π indicates an orbital perpendicular to this plane. The (non)planarity of the skeleton is measured by the dihedral angle CXCO.

TABLE 2: Relative Energies (kcal/mol) for Molecules or Ions Analogous to the Ionized 1,2-Ethanediol Isomers 8 and 9 and Their 1,4-H Shift Transition States[a]

	X	*iso*-**8**	TS	*iso*-**9**
case A	O	0 (σ), 14 (π)[b]	14 (0°)	−12 (σ)
	CH_2	0 (σ), 54 (π)	15 (0°)	−4 (σ)
case B	O	0 (π)	27 (30°)	−4 (78°)
	CH_2	0 (π)	26 (31°)	1 (180°)
	OH^+	0 (π), 21 (σ)	35 (29°)	−1 (50°)
	OCH_3^+	0 (π)	31 (28°)	−2 (163°)

[a] The orientation of the singly occupied orbital in *iso*-**8** and *iso*-**9** is indicated as σ or π (see text for details). The nonplanarity of the structures is indicated via the dihedral angle CXCO (between parentheses after TS and after *iso*-**9**). [b] π-Ionization of the ether oxygen is favored over that of the carbonyl oxygen.

SCHEME 4



The main feature of these results is that the stabilities of the two ionization states (σ or π) apparently reverse when we go from case A to case B. This may be an important factor in determining the magnitude of the activation energy for the H shift. In case A, the σ symmetry corresponds to the ground state, the transition state for the 1,4-H shift is planar, and the barrier is relatively low. However, in case B the π state is more stable than the σ state. This is a property of the radical O atom in both the neutral molecules and the cations. The 1,4-H shift is thus more difficult for case B, since here the molecule or ion has to be distorted before the shift can take place. This is further illustrated in Figure 2, which shows the transition-state structures for the 1,4-H shift in $CH_3OC(H){=}O^{\bullet+} \rightarrow {}^{\bullet}CH_2OC^+(H)OH$ (case A; X = O) and that for $CH_3O^+(H)CH_2O^{\bullet} \rightarrow {}^{\bullet}CH_2O^+(H)CH_2OH$ (case B; X = OH^+, TS **8** → **9** in Figure 1). It is seen that for case A, the dihedral angle is zero, while for case B, the ion is significantly distorted from planarity.

1,2-Propanediol. The sequence depicted in Scheme 3 (proposal A) has been the subject of a recent experimental and computational study,[15] and a brief discussion will suffice. Unlike 1,2-ethanediol, the reactions for 1,2-propanediol all take place below or at the dissociation limit;[12] that is, all species involved must have energies at or below that for $CH_3OH_2^+$ + $CH_3CO^{\bullet}$ = 0. First, the charge-transfer complex (CT) was located and its energy was calculated by the procedure described in ref 1. It was found that its energy lies just below (−1.7

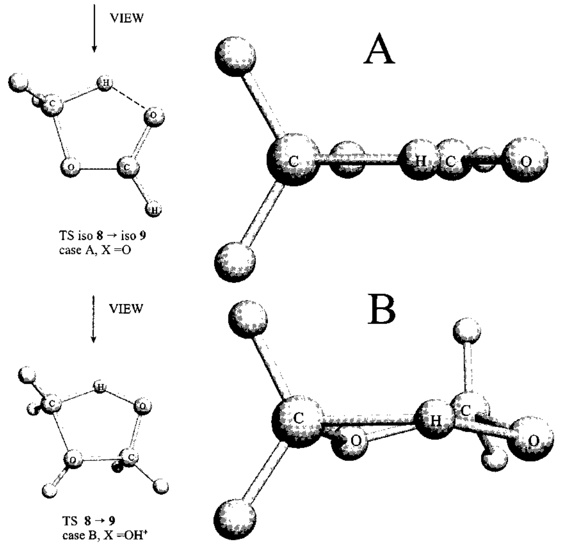


Figure 2. (A) Transition state for the 1,4-hydrogen shift in methyl formate: $CH_3OC(H){=}O^{\bullet+} \rightarrow {}^{\bullet}CH_2OC^{+}HOH$. (B) Transition state for the 1,4-hydrogen shift: $CH_3O^{+}(H)CH_2O^{\bullet} \rightarrow {}^{\bullet}CH_2O^{+}(H)CH_2OH$.

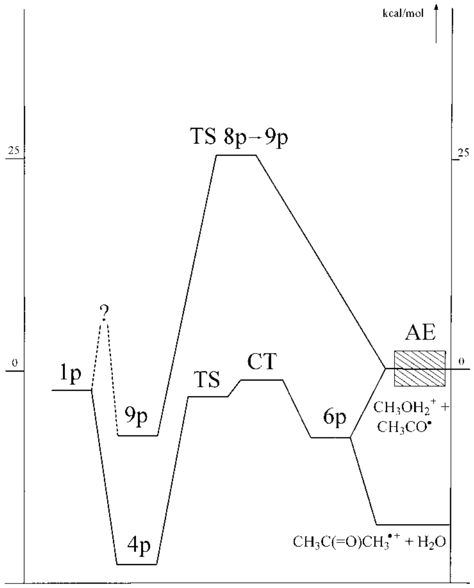


Figure 3. Theoretical results for the relative energies of isomers and transition states encountered in the dissociation of 1,2-propanediol radical cations according to Scheme 3.

kcal/mol) the above anchor point, and so charge transfer is energetically possible. For economical reasons (see ref 15), other relevant parts of the surface were calculated from UB3LYP/6-31G*-optimized geometries followed by single-point QCISD(T)/6-31G** calculations including the usual zero-point vibrational energy corrections. The obtained energies are given below in parentheses. The calculated energy diagram is given in Figure 3. As with 1,2-ethanediol, ions **1p**, formed by vertical ionization of 1,2-propanediol, collapse to the long-bonded species **3p** (−15.9 kcal/mol), which has a C−C bond length of 1.964 Å (see Scheme 3). The species can undergo reorientation to form the hydrogen-bridged species **4p** (−20.7 kcal/mol). Because the proton affinity of acetaldehyde is greater than that of $CH_2OH^{\bullet}$, while that of formaldehyde is smaller than that of $CH_2OH^{\bullet}$, the proton will now be closer to acetaldehyde (compare **4p** (Scheme 3) and **4** (Scheme 1)). Ions **4p** may then shuttle[8] the bridging proton to the methylene carbon, TS (−4.4 kcal/mol, RHF/D95**-optimized geometry; see ref 15). Next, the charged methanol rotates around the acetaldehyde molecule until a configuration is reached (CT) where the oxygen lone pairs are oriented toward each other so that charge transfer is possible. Now, the neutral methanol in turn can migrate within the electrostatic field of the charged acetaldehyde such that proton transfer is possible to generate **6p** (−8.5 kcal/mol, RHF/D95**-optimized geometry; see ref 15), which then dissociates. Note that all these transformations take place below the dissociation limit, and so the ion−dipole mechanism is energetically possible.

With respect to the distonic ion mechanism, the barrier for the transformation **9p** → **8p** was determined by a QCISD(T)/6-31G** calculation as 25.5 kcal/mol above the dissociation threshold ($CH_3OH_2^{+} + CH_3CO^{\bullet}$). Thus, this transformation takes place far above the dissociation limit, and so the distonic ion mechanism can be ruled out for the low-energy ions.

In summary, the above computational results show that the rearrangement processes observed in the radical cations of 1,2-ethanediol and 1,2-propanediol can best be understood in terms of proton and electron transfers taking place in ion−dipole complexes rather than hydrogen atom shifts in distonic ions. Thus, the sequential transfer of a proton and an electron in ion−dipole complexes appears much more "economical" than a prompt hydrogen atom shift in a distonic ion.

Why Only One Fragmentation for Ionized 1,2-Ethanediol? Our computational results allow a comparison of the dissociation behavior of ionized 1,2-ethanediol and 1,2-propanediol (compare Figures 1 and 3). As was stated above, $CH_3OH_2^{+}$ and $HCO^{\bullet}$ are the sole dissociation products for ionized 1,2-ethanediol. By contrast, 1,2-propanediol undergoes, in addition to loss of $CH_3CO^{\bullet}$, five other dissociations.[12,15] Apparently, the additional methyl substituent makes available dissociation routes and products that are not possible for ionized 1,2-ethanediol.[15] However, there is one abundant dissociation observed for ionized 1,2-propanediol, namely, the loss of H_2O, which, too, should occur easily for ionized 1,2-ethanediol but which is nevertheless not observed. For **1p** the reactions proposed to occur from **6p** via a proton shift followed by a "methyl cation shuttle"[16] to produce ionized acetone[15] are (R = CH_3)

$$\mathbf{1p} \rightarrow O{=}C(R){-}H^{\bullet+}\cdots H{-}O(H)CH_3\ (\mathbf{6p}) \rightarrow$$
$$R{-}C^{\bullet}{=}O\cdots H{-}O(H)CH_3^{+}\ (\mathbf{11p}) \rightarrow$$
$$R{-}C^{\bullet}{=}O\cdots CH_3^{+}{-}OH_2\ (\mathbf{12p}) \rightarrow$$
$$R{-}C^{\bullet}({=}O)\cdots CH_3^{+}{-}OH_2\ (\mathbf{13p}) \rightarrow$$
$$R{-}C^{\bullet}({=}O){-}CH_3^{+}\cdots OH_2\ (\mathbf{14p}) \rightarrow$$
$$R{-}C({=}O){-}CH_3^{\bullet+} + H_2O$$

Rotation of the charged $CH_3OH_2^{+}$ group in **11p** leads to the methyl cation bridged species **12p** after which the methyl cation shuttles to the carbon atom of $R{-}C^{\bullet}{=}O$ followed by dissociation of the intermediate ion−dipole complex **14p**. As can be seen from Figure 3, for ionized 1,2-propanediol these products lie below the anchor point $CH_3OH_2^{+} + CH_3CO^{\bullet}$, but the same is true for ionized 1,2-ethanediol (see Figure 1), yet loss of water is not observed. Our ab initio calculations provide an explanation for this puzzling result. According to our results, ions **6p** lie below the anchor point (see Figure 3); that is, proton transfer is endothermic. Hence, the resulting ions **11p** live sufficiently long to undergo other transformations such as a "methyl cation shuttle". By contrast, ions **6** lie above the anchor point (see Figure 1), and so proton transfer now is exothermic and fast. Therefore, ions **11**, $H{-}C^{\bullet}{=}O\cdots H{-}O(H){-}CH_3^{+}$, have a fleeting existence only and cannot undergo other transformations. A confirmation of these findings is provided by an assessment of the stabilization energies (SE) of ions **6** and **6p**. Using $\sum\Delta H_f[CH_3OH_2^+ + HCO^\bullet] = 144$ kcal/mol,[17] we calculate, using the results of Table 1, $\Delta H_f = 152$ kcal/mol for ions **6**. Using $\Delta H_f[CH_2O^{\bullet+}] = 225$ kcal/mol [17] and $\Delta H_f[CH_3OH^{\bullet+}] = -48$ kcal/mol,[17] we obtain an SE(**6**) of 25 kcal/mol. A similar procedure for ions **6p** (using $\Delta H_f[CH_3OH_2^+ + CH_3CO^\bullet] = 132$ kcal/mol [17] and $\Delta H_f[CH_3CHO^{\bullet+}] = 196$ kcal/mol [17]) yields SE-(**6p**) = 26 kcal/mol. Not only are these SE's entirely reasonable in magnitude, they are also equal. The reason that many of the intermediates and transition states for ionized 1,2-propanediol lie below the anchor point is that these ionic intermediates are stabilized by the additional methyl group, but the product ion $CH_3OH_2^+$ obviously is not.

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Supporting Information Available: RHF/DZP-optimized geometries for the minima and transition states listed in Table 2 (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Burgers, P. C.; Ruttink, P. J. A. R. *Org. Mass Spectrom.* **1993**, *28*, 1087.

(2) Burgers, P. C.; Holmes, J. L.; Hop, E. C. A.; Postma, R.; Ruttink, P. J. A. R.; Terlouw, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7315.

(3) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. See also the following. Morton, T. H. *Org. Mass Spectrom.* **1992**, *27*, 353. Biermann, H. W.; Morton, T. H. *J. Am. Chem. Soc.* **1983**, *105*, 5025.

(4) Yates, B. F.; Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1987**, 207.

(5) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805.

(6) Cao, J. R.; George, M.; Holmes, J. L.; Sirois, M.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1992**, *114*, 2017.

(7) Audier, H. E.; Millet, A.; Leblanc, D.; Morton, T. H. *J. Am. Chem. Soc.* **1992**, *114*, 2020.

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

(9) For recent reviews and leading references see the following. (a) Radom, L.; Gauld, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 9831. (b) Chalk, A. J.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 7573.

(10) (a) Mourges, P.; Audier, H. E.; Leblanc, D.; Hammerum, S. *Org. Mass Spectrom.* **1993**, *28*, 1098. (b) Audier, H. E.; Leblanc, D.; Mourges, P.; McMahon, T. B.; Hammerum, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2329.

(11) Gauld, J. W.; Audier, H. E.; Fossey, J.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 6299.

(12) Van Baar, B. L. M.; Burgers, P. C.; Holmes, J. L.; Terlouw, J. K. *Org. Mass Spectrom.* **1988**, *23*, 355.

(13) (a) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem.* **1977**, *11*, 149. Saunders V. R.; van Lenthe J. H. *Mol. Phys.* **1983**, *48*, 923. (b) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*; Gaussian Inc: Pittsburgh, 1996.

(14) Heinrich, N.; Schmidt, J.; Schwarz, H.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1317.

(15) Burgers, P. C.; Fell, L. M.; Milliet, A.; Rempp, M.; Ruttink, P. J. A. R.; Terlouw, J. K. *Int. J. Mass Spectrom. Ion Processes* **1997**, *166*/*167*, 291.

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

(17) Lias, S.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).