for oscillation has even found its way into widely used textbooks of physical chemistry.[37] It is important to bear in mind that self-inhibition provides another form of feedback that can lead to chemical oscillation. While this is the first self-inhibitory chemical oscillator of which we are aware, it is likely that there are many more oscillatory reactions based on self-inhibition that are waiting to be discovered.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8800169) and by a U.S.-Hungarian cooperative grant from the NSF and the Hungarian Academy of Sciences. We thank Patrick De Kepper and Harry Swinney for useful discussions and for sharing their results with us prior to publication.

---

[37] Atkins, P. W. *Physical Chemistry*, 3rd ed.; Freeman: New York, 1986; p 728.

Role of Ion-Neutral Complexes during Acid-Catalyzed Dehydration of Ethanol in the Gas Phase

Guy Bouchoux* and Yannik Hoppilliard

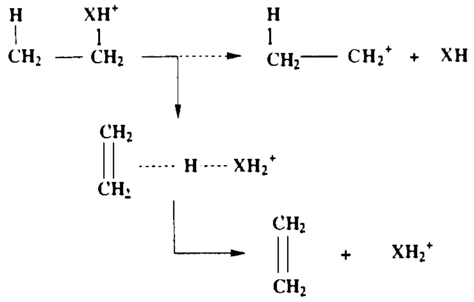
Contribution from the Département de Chimie, Laboratoire des Mécanismes Réactionnels, Ecole Polytechnique, 91128 Palaiseau Cedex, France.

Received April 23, 1990. Revised Manuscript Received July 6, 1990

Abstract: Acid-catalyzed dehydration of ethanol in the gas phase has been studied both theoretically and experimentally. Molecular orbital calculations have been done at the MP3/6-31G*//6-31G* level with correction of the zero-point vibrational energy. Protonated ethanol, **1** is predicted to isomerize easily into the $C_2H_4\cdots H\cdots OH_2^+$ complex, **2** (activation energy 120 kJ/mol). This result is in agreement with the observation of a near statistical hydrogen exchange preceding the dehydration reaction **1** → $C_2H_4 + H_3O^+$. In the case of the water-solvated ion $C_2H_5OH_2\cdots OH_2^+$, **5**, isomerization into a proton-bound complex $C_2H_4\cdots H_5O_2^+$, **6**, needs a larger amount of energy (ca. 180 kJ/mol). Again the calculations agree with experiments: the important activation energy for the process **5** → **6** prevents hydrogen exchanges and ethene elimination. Extension of these conclusions to higher systems is discussed.

1,2 elimination reactions are of fundamental interest in organic chemistry and are ubiquitous processes in gas-phase chemistry of cationic or anionic species. For such reactions, some mechanistic proposals presently encountered in the literature involve ion-neutral complexes, i.e., species in which noncovalent interactions retain close together two entities able eventually to react unimolecularly or bimolecularly, as key intermediates.[1-3] In the case of a protonated species, a suggested dissociation mechanism implies formation of an elusive proton-bound complex as summarized in Scheme I.

Scheme I



Starting from $CH_3CH_2XH^+$, the direct C-X bond elongation leads to the products $C_2H_5^+$ and XH. During this process, interaction between these two products may give rise to a proton-bound intermediate which, in turn, decomposes into $C_2H_4 + XH_2^+$.

Dehydration of protonated alcohols is a common type of elimination reaction whose description may enter into this frame. The purpose of the present work is to test the validity of Scheme I in providing a reasonable view of the potential energy surface associated with dehydration of protonated alcohols in the gas phase. Therefore, investigations on the prototype systems $C_2H_5OH_2^+$ ($C_2H_5OH_2^+$, H_2O and $C_2H_5OH_2^+$, C_2H_5OH) have been done by means of molecular orbital calculations and comparison has been made with mass spectrometry experiments.

I. Dehydration of Protonated Ethanol

In the gas-phase $C_2H_5OH_2^+$, **1**, may be produced by protonation of ethanol under chemical ionization conditions[4-10,19-21,31] or by condensation reaction between $C_2H_5^+$ ions (coming, for example, from C_2H_5Br) and a water molecule.[8]

---

[1] McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363.

[2] Bouchoux, G. *Adv. Mass Spectrom.* **1989**, *11*, 812.

[3] (a) Burgers, P. C.; Terlouw, J. K. In *Specialist Periodical Reports: Mass Spectrometry*; Rose, M. E., Ed.; The Royal Society of Chemistry: London, 1989; Vol. 10, Chapter 2. (b) Heinrich, N.; Schwarz, H. In *Ion and Cluster Ion Spectroscopy and Structures*; Maier, P., Ed.; Elsevier: Amsterdam, 1989; p 329. (c) Tuma, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 2714.

[4] Colosimo, M.; Branacaleoni, E. *Org. Mass Spectrom.* **1982**, *17*, 286.

[5] Jarrold, M. F.; Illies, A. J.; Kirchna, N. J.; Bowers, M. T. *Org. Mass Spectrom.* **1983**, *18*, 388.

[6] Dawson, P. H. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *50*, 287.

[7] Jarrold, M. F.; Kirchner, N. J.; Lin, S.; Bowers, M. T. *J. Phys. Chem.* **1986**, *90*, 78.

[8] Harrison, A. G. *Org. Mass Spectrom.* **1987**, *22*, 637.

[9] Siek, L. W.; Abramson, F. P.; Futrell, J. H. *J. Chem. Phys.* **1966**, *45*, 2859.

[10] (a) Beauchamp, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 5925. (b) Beauchamp, J. L.; Case, M. *J. Am. Chem. Soc.* **1972**, *94*, 2638. (c) Beauchamp, J. L.; Caserio, M.; McMahon, T. B. *J. Am. Chem. Soc.* **1974**, *96*, 6243.

[11] (a) Bohme, D. K.; Mackay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 2173. (b) Collyer, S. M.; McMahon, T. B. *J. Phys. Chem.* **1983**, *87*, 909.

[12] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

[13] Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *Gaussian 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

[14] (a) Jones, W. H.; Mezey, P. G.; Csizmadia, I. G. *J. Mol. Struct. (THEOCHEM)* **1985**, *121*, 85. (b) Cao, H. Z.; Allavena, M.; Tapia, O.; Evleth, E. M. *Chem. Phys. Lett.* **1983**, *96*, 458.

[15] Reiner, E. J.; Poirier, R. A.; Peterson, M. R.; Csizmadia, I. G.; Harrison, A. G. *Can. J. Chem.* **1986**, *64*, 1652.

[16] See, for example: Matsuura, K.; Nunome, K.; Toriyama, K.; Iwasaki, M. *J. Phys. Chem.* **1989**, *93*, 149.

0002-7863/90/1512-9110$02.50/0

Long-lived ions **1** (lifetime of ca. 10^{-5} s) dissociate unimolecularly by elimination of an ethylene molecule following reaction a:

$$C_2H_5OH_2^+ \rightarrow H_3O^+ + C_2H_4 \qquad (a)$$

This fragmentation is accompanied by a very low kinetic energy release ($T_{0.5}$ = 2.5 meV;[7] $T_{0.5}$ = 3.2 meV, this work), suggesting no appreciable energy barrier for the reverse reaction. The temperature dependence of the reaction rate supports this conclusion.[31] Partially deuterated species $C_2H_5OHD^+$ [7] and $C_2H_5OD_2^+$ [8] give H_2DO^+/H_3O^+ (ratio of metastable peak height 25/75; statistical ratio 29/71) and $HD_2O^+/H_2DO^+/H_3O^+$ (ratio of metastable peak height 12/43/45; statistical ratio 14/57/29), respectively. Our results from protonated CH_3CD_2OH and CD_3CH_2OH give $HD_2O/H_2DO/H_3O$ of 10/42/48 (statistical ratio 14/57/29) and $D_3O/HD_2O/H_2DO/H_3O$ of 4/25/46/25 (statistical ratio 3/34/51/11), respectively. A substantial H/D scrambling is thus associated with process a when ions **1** of low internal energy are sampled.

The CID (collision-induced dissociations) spectrum of **1** has been studied under low[6,8] or high[5,7] collision energy. In both experiments, it is observed that the loss of a water molecule (process b) competes with reaction a.

$$C_2H_5OH_2^+ \rightarrow C_2H_5^+ + H_2O \qquad (b)$$

At very low collision energies (less than 5 eV) H_3O^+ formation (process a) dominates, in agreement with its lowest enthalpy requirement (see later). The increase in collision energy is followed by the increase of $C_2H_5^+$ ion abundance until reaching a stationary situation. At 8 keV of collision energy the ratio of peak height $C_2H_5^+/H_3O^+$ attains 1.2.[5,7] The CID spectra of variously deuterated ions **1** obtained at 10 eV collision energy demonstrate the following trends: for process a, a pronounced H/D exchange is observed but equilibration is not complete and H_3O^+ ions bring one hydrogen preferentially from the original methyl group; for process b, H/D exchange is also important but less than for reaction a, a preference is observed for the direct C–O bond cleavage.

Information regarding the proton-bound complex $CH_2CH_2 \cdots H_3O^+$, **2**, is less abundant. The formation of a cluster ion like **2** has been proposed to compete with the proton-transfer reaction: $C_2H_4 + H_3O^+ \rightarrow C_2H_5^+ + H_2O$.[11] The cluster, produced by chemical ionization of a mixture of C_2H_4 and H_2O in a buffer bath of Ar, gives a CID spectrum very close to that of protonated ethanol.[7] This observation suggests partial loss of structural identity for **1** and **2** below their fragmentation threshold of lowest energy.

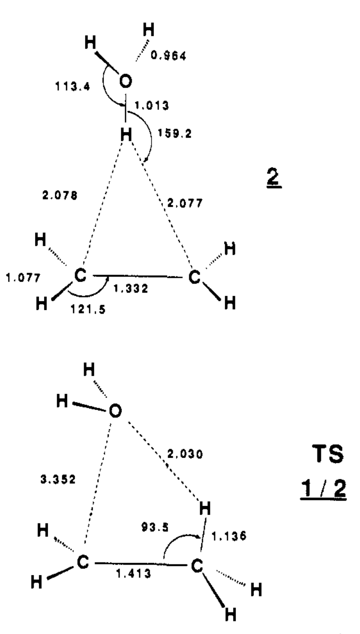


Figure 1. Optimized (6-31G*) structures of $C_2H_7O^+$ ions.

Table I. Total Energies (Hartree) and Corrected Zero-Point Vibrational Energies (ZPVE, kJ/mol) of $C_2H_7O^+$ Ions[a]

	species	6-31G*//6-31G*[b]	MP2/6-31G*// 6-31G*[b]	ZPVE
1	$C_2H_5O^+H_2$ (anti)	−154.387 157 (0)	−154.822406 (0)	234
2	$C_2H_4 \cdots HOH_2$	−154.349 409 (99)	−154.791382 (81)	222
	TS **1–2**	−154.344 915 (111)	−154.768508 (142)	212
	$C_2H_5^+$ (class.)	−78.311 227	−78.542888	152
	$C_2H_5^+$ (bridged)	−78.309 943	−78.551840	154
	H_2O	−76.010 746	−76.195960	54
3	$C_2H_5^+$ (b) + H_2O	−154.320 689 (175)	−154.747800 (196)	208
	C_2H_4	−78.031 719	−78.284345	129
	H_3O^+ (C_{3v})	−76.289 338	−76.473822	87
4	$C_2H_4 + H_3O^+$	−154.321 057 (174)	−154.758167 (169)	216

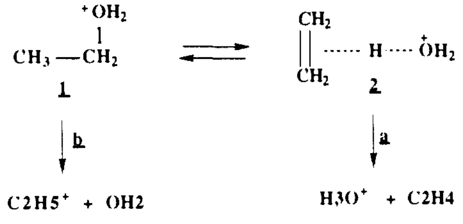
[a] Optimized 6-31G* geometries. [b] Numbers in parentheses, relative energies (kJ/mol).

Table II. Calculated and Experimental Relative Energies of $C_2H_7O^+$ Ions (kJ/mol)

species	$E_{\mathrm{rel,calc}}$[a]	$\Delta H_{\mathrm{exp}}°$ ($\Delta H_f°$)[b]
1 $C_2H_5OH_2^+$	0	0 (507)
2 $C_2H_4 \cdots HOH_2^+$	69	
3 $C_2H_5^+ + H_2O$	170[c]	153 (660)
4 $C_2H_4 + H_3O^+$	151	132 (643)
1/2 TS	120	<132

[a] Relative energies calculated by using MP2/6-31G*//6-31G* computations corrected by ZPVE(6-31G*) contributions. The most stable (bridged) structure has been considered for the $C_2H_5^+$ cation. [b] Experimental 298 K heats of formation indicated in the parentheses have been obtained from $\Delta H_f°$ = 52, −242, and −235 kJ/mol for C_2H_4, H_2O, and C_2H_5OH, respectively. Proton affinity values used to derive $\Delta H_f°(MH^+)$ are 680, 701, and 788 [reference PA (NH_3) = 853 kJ/mol) for C_2H_4, H_2O, and C_2H_5OH, respectively, thus giving $\Delta H_f°(C_2H_5^+)$ = 902 kJ/mol, $\Delta H_f°(H_3O^+)$ = 587 kJ/mol, and $\Delta H_f°(C_2H_5OH_2^+)$ = 507 kJ/mol [$\Delta H_f°(H^+)$ = 1530 kJ/mol]. [c] $C_2H_5^+$ bridged structure.

In summary, and as suggested by the available experimental data, the behavior of ions **1** and **2** may be rationalized by the following scheme:



The detailed mechanism of the isomerization **1** ⇌ **2** and the associated potential energy profile will be now examined theo-

---

(17) Smith, D.; Adams, N. G.; Henchman, M. J. *J. Chem. Phys.* **1980**, *72*, 4951.

(18) Schwarz, H.; Stahl, D. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 285.

(19) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

(20) Hiraoka, K.; Takimoto, H.; Morise, S. K. *J. Am. Chem. Soc.* **1986**, *108*, 5683.

(21) (a) Iraqi, M.; Lifshitz, C. *Int. J. Mass Spectrom. Ion Phys.* **1989**, *88*, 45. (b) Morgan, S.; Keesee, R. G.; Castelman, A. W. Jr. *J. Am. Chem. Soc.* **1989**, *111*, 3841.

(22) Raghavachari, K.; Chandrasekhar, J.; Burnier, R. C. *J. Am. Chem. Soc.* **1984**, *106*, 3124.

(23) McMahon, T. B.; Beauchamp, J. L. *J. Phys. Chem.* **1977**, *81*, 593.

(24) Graul, S. T.; Squires, R. R. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *81*, 183.

(25) (a) Audier, H. E.; Monteiro, C.; Mourgues, P.; Robin, D. *Commun. Mass Spectrom.* **1989**, *3*, 84. (b) Audier, H. E.; Monteiro, C.; Robin, D. *Org. Mass Spectrom.* **1989**, *24*, 146. (c) Audier, H. E.; Monteiro, C.; Mourgues, P.; Robin, D. *Org. Mass Spectrom.* **1989**, *24*, 289.

(26) Hiraoka, K.; Takimoto, H.; Yamabe, S. *J. Phys. Chem.* **1986**, *90*, 5910.

(27) Mori, Y.; Kitayawa, T. *Chem. Phys. Lett.* **1986**, *128*, 383, 389.

(28) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195.

(29) Karpas, Z.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1989**, *93*, 1859.

(30) Sheldon, J. C.; Currie, G. J.; Bowie, J. H. *J. Chem. Soc. Perkin Trans. 2* **1986**, 941.

(31) Meot-Ner (Mautner), M. Sieck, L. W. *Int. J. Mass Spectrom. Ion Processes* **1989**, *92*, 123.

(32) Curtiss, L. A.; Blander, M. *Chem. Rev.* **1988**, *88*, 827.

retically by ab initio molecular orbital calculations.

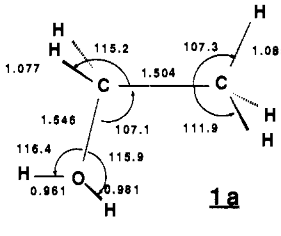
Molecular Orbital Calculations. Molecular orbital calculations have been undertaken at the ab initio level with the split valence polarized 6-31G* basis set of atomic orbitals. Stable structures **1** and **2** have been optimized without symmetry constraints. Complete analysis of the force constant matrix was done in order (i) to fully characterize minima and saddle points on the potential energy surface and, (ii) to calculate the zero-point vibrational energy (ZPVE) of each species.

Energy calculations were improved by including electron correlation corrections by means of the Moller–Plesset perturbation theory performed at the second order. A scale factor of 0.9 has been applied to the calculated ZPVE in order to account for the overestimation of the vibrational frequencies at the Hartree-Fock level.[12]

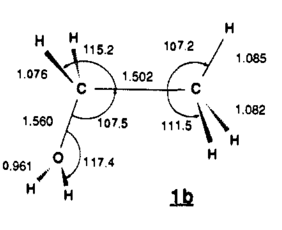
All calculations have been carried out by using the GAUSSIAN86 series of programs.[13]

Geometries (6-31G*) are displayed in Figure 1; total and relative energies calculated at various levels of theory are quoted in Tables I and II. In the latter, a comparison is made with the experimental variations of enthalpy.

The most stable conformation for ion **1** is offered by **1a**; structure **1b** possesses a negative eigenvalue in its diagonalized force constant matrix, corresponding to rotation of the OH_2 group along the C–O bond axis. The calculation showed that during protonation on the oxygen atom the C–O bond is lengthened from 1.404 to 1.546 Å, as predicted by the 6-31G* calculations.



1a



1b

During the geometry optimization of ion **2**, only one minimum was located for the proton-transfer reaction between H_2O and $CH_2{=}CH_2$ in which the proton is bound to the most basic site. This result confirms an earlier conclusion drawn from STO-3G molecular orbital calculation.[14] The two bond lengths most affected by the clustering are OH (0.961 Å in H_3O^+, 6-31G* optimized geometry) and C=C (1.371 Å in $CH_2{=}CH_2$, 6-31G* optimized geometry). Our best estimate (MP2/6-31G*//6-31G*+ZPVE) predicts a stabilization energy of **2** with respect to its separated components **4**, $C_2H_4 + H_3O^+$, equal to 82 kJ/mol.

The transition state **1/2** looks like a loose association between a classical $C_2H_5^+$ cation and a molecule of water with a calculated stabilization energy of 70 kJ/mol. This situation is reminiscent of the case of protonated isopropylamine.[15]

The potential energy diagram associated with Scheme I is presented in Figure 2.

A prominent result of the calculation is the fact that transition state **1/2** lies below the fragments $C_2H_4 + H_3O^+$, **4**. This situation explains perfectly the small release of kinetic energy associated with the formation of H_3O^+ from **1**. Ions **1**, metastable toward this fragmentation, are in fact vibrationally excited complexes **2**. Such loosely bound species are not expected to dissociate with the release of a great amount of kinetic energy.

Figure 2 also offers clear support for the discussion concerning the H/D scrambling observed during the dissociation of deuterated ions **1**. Free rotation of the methyl group (assumed to need around 10 kJ/mol[16]) and reversible isomerization **1** ⇌ **2** render equivalent the five hydrogen atoms of the ethyl group for ions **1** containing at least 120 kJ/mol of internal energy. The involvement, in the H/D scrambling, of the two hydrogens linked to the oxygen atom is attested to by experiment. It implies a "free" rotation of the OH_3^+ moiety inside complex **2**. The situation is similar to that of the $H_2O{\cdots}H_3O^+$ complex in which the hydronium ion apparently turns easily.[17]

Finally, one should note that rearrangements of the type **1** → **2** may also explain the isomerization of the protonated form of higher homologues of ethanol.[18]

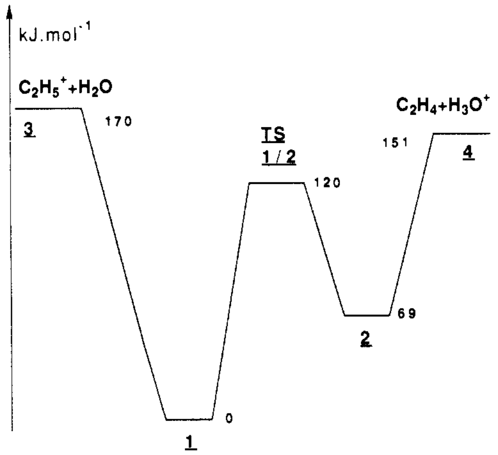


Figure 2. Calculated (MP2/6-31G*//6-31G* + ZPVE) relative energies of $C_2H_7O^+$ ions.

II. Dehydration of Protonated Ethanol, Water Cluster

The general trend of protonated ROH, H_2O clusters is to eliminate a water molecule[19–21] or to generate the corresponding alkene molecule (R–H).[19] Only the former process is efficient for R = C_2H_5, and from this point of view, ethanol seems to constitute a particular case.

Hydration reaction of protonated ethanol (reaction c) has been studied in pulsed electron beam mass spectrometers under high-pressure source conditions,[19,20]

$$C_2H_5OH_2^+ + H_2O \rightarrow (C_2H_5OH, H_2O)H^+ \qquad (c)$$

From measurement of equilibrium constants at various temperatures the enthalpy change for reaction c has been estimated to be 100[19]–111[20] kJ/mol.

Hiraoka et al. (*20*) noted that the acid-catalyzed dehydration reaction d

$$C_2H_5OH_2^+ + H_2O \rightarrow C_2H_4 + H_5O_2^+ \qquad (d)$$

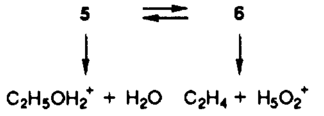
could not be detected even though this process is slightly exothermic (ΔH = 4 kJ/mol). This situation is puzzling in view of the case of protonated *tert*-butyl alcohol[19] for which the formation of isobutene, by a reaction similar to d, is observed while the reaction is endothermic by 34 kJ/mol.

We observed that the $(C_2H_5OH,H_2O)H^+$ cluster may be produced by self chemical ionization of the ethanol/water mixture. Metastable ions m/z 65 dissociate only by one route:

$$(C_2H_5OH, H_2O)H^+ \rightarrow C_2H_5OH_2^+ + H_2O \qquad (e)$$

This reaction is accompanied by a small kinetic energy release, $T_{0.5}$ = 5.5 meV. When partially deuterated ethanol CH_3CD_2OH and CD_3CH_2OH is used, it is observed that the water loss (reaction e) is not preceded by a significant H/D exchange between carbon- and oxygen-bonded isotopes. Accordingly, the clusters $(CD_3CH_2OH, H_2O)H^+$ and $(CD_3CH_2OH, H_2O)H^+$ eliminate exclusively H_2O in the metastable time frame.

Molecular Orbital Calculations. In order to understand the special behavior of protonated ethanol/water cluster, the following system has been theoretically investigated:



All the geometries have been optimized with the 6-31G* basis set of atomic orbitals; resulting structures are displayed in Figure 3. Total and relative energies of **5-12** are reported in Tables III and IV.

Concerning the energetic data, a good agreement is found between theory and experiment. The stabilization energy of the

Table III. Total Energies (Hartree) and Corrected Zero-Point Vibrational Energies (ZPVE, kJ/mol^{-1}) of $C_2H_9O_2^+$ Ions[a]

	species	6-31G*//6-31G*	MP2/6-31G*//6-31G*	ZPVE
5	$C_2H_5OH_2\cdots OH_2^+$	−230.438751 (0)[b]	−231.065930 (0)[b]	296
6	$C_2H_4\cdots HOH_2\cdots OH_2^+$	−230.404276 (91)	−231.036347 (78)	284
	TS **5–6**$^+$	−230.376168 (164)	−230.990265 (199)	275
7	**1** + H_2O^+	−230.397903 (107)	−231.018366 (125)	288
	C_2H_4	−78.031719	−78.284345	129
	$H_2O\cdots H\cdots OH_2^+$	−152.352487	−152.729349	146
8	$C_2H_4 + H_5O_2^+$	−230.384166 (143)	−231.013694 (137)	275
9	**2** + H_2O	−230.360155 (206)	−230.987342 (206)	276
10	$C_2H_4 + H_3O^+ + H_2O$	−230.331803 (281)	−230.954127 (294)	270
	$H_2O\cdots H_2O$	−152.030403	−152.403277	117
	$C_2H_5^+$ bridged	−78.309943	−78.551840	154
11	$C_2H_5^+ + H_2O\cdots H_2O$	−230.340346 (258)	−230.955117 (291)	271
12	$C_2H_5OH + H_3O^+$	−230.365080 (193)	−230.98944 (201)	290

[a] Optimized 6-31* geometries. [b] Numbers in parentheses, relative energies (kJ/mol).

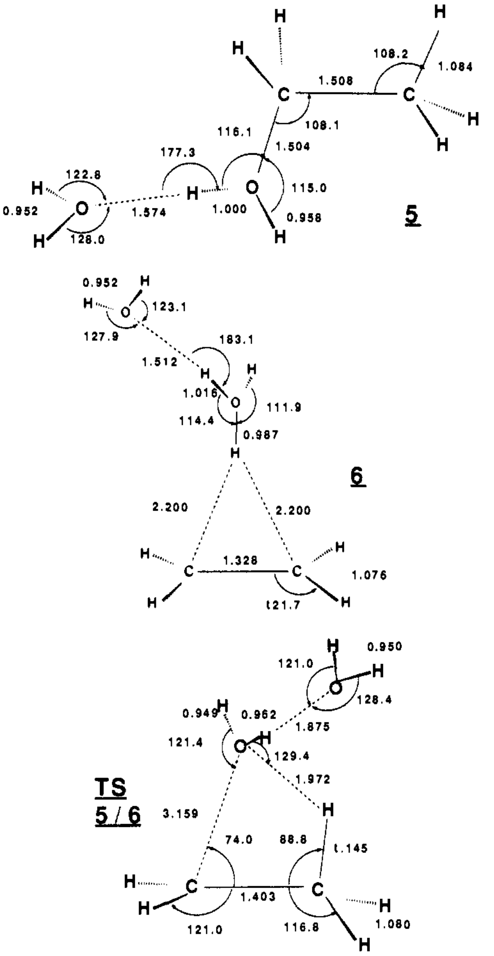


Figure 3. Optimized (6-31G*) structures of $C_2H_9O_2^+$ ions.

proton-bound complexes **5** and $H_2O\cdots H\cdots OH_2^+$ with respect to their isolated components are reproduced within ca. 10 kJ/mol. One should note also that, in the case of **5**, our result (117 kJ/mol) is close to the MP3/6-31G**//3-21G value (113 kJ/mol) calculated by Raghavachari et al.[22]

With respect to protonated ethanol **1**, the proton-bound complex **5** is characterized (i) by a shortening of the C–O bond length (1.504 vs 1.546 Å in **1**) and (ii) by a stretching of the O–H bond supporting the proton linkage (1.000 vs 0.961 Å in **1**). The hydrogen-bond length (1.574 Å) is larger than that occurring between H_2O and H_3O^+ in $H_5O_2^+$ (1.410 Å). This difference is in close relation with the corresponding stabilization energy of the two complexes: the calculated values (Tables III and IV) are 117 and 152 kJ/mol for **5** and $H_5O_2^+$, respectively.

Structure **6** is comparable to the hydrogen-bridged complex **2**. The second water molecule is efficiently retained by an extra hydrogen bond (length 1.512 Å; energy 120 kJ/mol). One may observe that the central H_3O^+ moiety is slightly moved away from the ethylene molecule in **6** by approximatively 0.2 Å. Thus, it is not surprising that the dissociation energy is lower for **6** → **8** (50 kJ/mol) than for **2** → **4** (82 kJ/mol).

Again, the transition state **5/6** connecting the oxygen-protonated species **5** and the proton-bound complex **6** may be seen as a loose

Table IV. Calculated and Experimental Relative Energies of $C_2H_9O_2^+$ Ions (kJ/mol)

	species	$E_{rel,calc}$[a]	$\Delta H_{exp}°$	$(\Delta H_f°)$[b]
5	$C_2H_5OH_2\cdots OH_2^+$	0	0	(160)[c]
6	$C_2H_4\cdots HOH_2\cdots OH_2^+$	66		
	TS 5–6	178	>105	(>265)
7	$C_2H_5OH_2^+ + H_2O$	117	105 ± 6	(265)
8	$C_2H_4 + H_5O_2^+$	116	101 ± 12	(261 ± 6)[d]
9	**2** + H_2O	186	180 ± 6	(340)[e]
10	$C_2H_4 + H_3O^+ + H_2O$	268	237 ± 6	(397)
11	$C_2H_5^+ + H_4O_2$	266	238 ± 12	(398 ± 6)
12	$C_2H_5OH + H_3O^+$	195	192 ± 6	(352)

[a] See Table II. [b] See Table II. [c] $\Delta H_f°(C_2H_5OH_2\cdots OH_2)^+ = \Delta H_f°(C_2H_5OH_2)^+ \Delta H_{assn}°$ with, for the latter, a value between 100[19] and 111 kJ/mol.[20] [d] $\Delta H_f°(H_5O_2^+) = \Delta H_f°(H_2O) + \Delta H_f°(H_3O^+) = \Delta H_{assn}°$ with, for the latter, a value between 146[26] and 134 kJ/mol.[19] [e] The stabilization energy of **2** is coming from the calculations quoted in Tables I and II. [f] By use of $\Delta H_f°(C_2H_5^+) = 902$, $\Delta H_f°(H_2O) = -242$ kJ/mol and $\Delta H_{stab}° = 15–24$ kJ/mol for the (H_2O) association.[32]

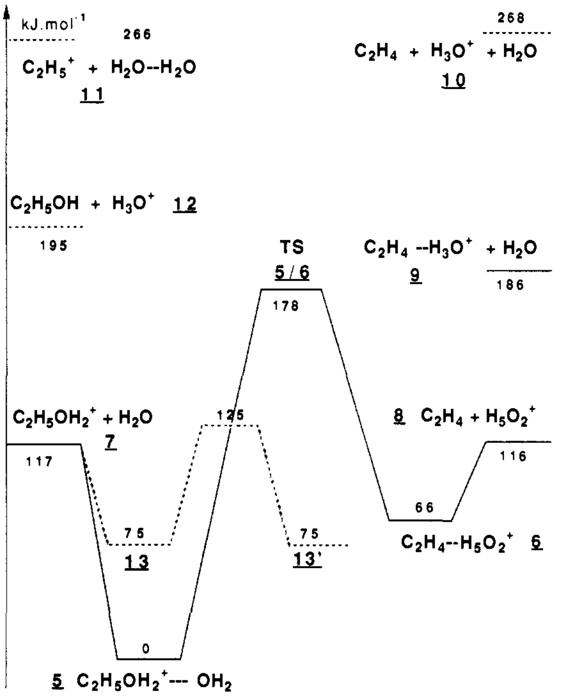


Figure 4. Calculated (MP2/6-31G*//6-31G* + ZPVE) relative energies of $C_2H_9O_2^+$ ions.

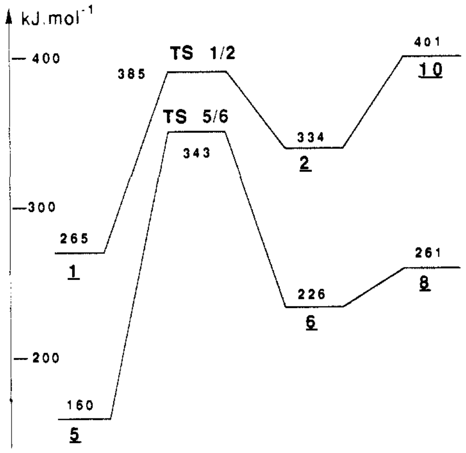


Figure 5. Comparative potential energy surfaces for dehydration reactions of ethanol.

association between a classical ethyl cation and, here, a water dimer. The complexation energy is predicted to be higher by roughly 20 kJ/mol than for transition state **1**/**2**.

Relative energies of the various species **5**–**12** are illustrated on Figure 4. The dotted lines correspond to the ion–dipole complex **13** and its degenerate rearrangement, which has been presented in the literature (MP3/6-31G**//3-21G values).[22]

From examination of Figure 4 it is obvious that hydrogen-bonded complexes **5** containing internal energy between 117 (experimentally 105 kJ/mol) and 178 kJ/mol cannot dissociate by a route other than the water elimination giving $C_2H_5OH_2^+$ + H_2O, **7**. In this energy range, no isomerization into **6** is possible and consequently no dehydration reaction leading to C_2H_4 + $H_5O_2^+$, **8**, is allowed. The specific elimination of a water molecule containing none of the hydrogen atoms present in the ethyl group is also explainable in a similar way. However, the results of Raghavachari et al.[22] indicate that the interconversion

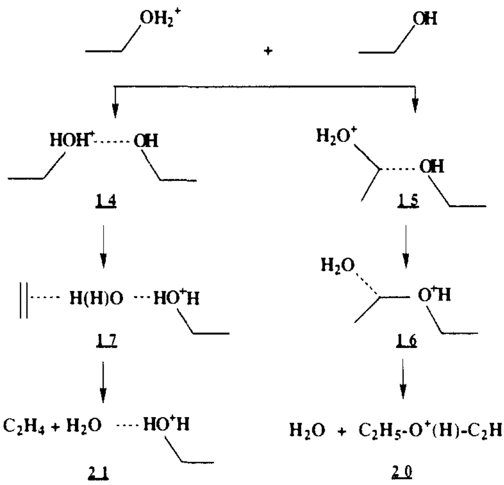
$$\underset{\mathbf{13}}{H_2O\cdots C_2H_5OH_2^+} \rightarrow \underset{\mathbf{13'}}{H_2OC_2H_5\cdots OH_2^+}$$

via a S_N2 process needs only 50 kJ/mol. The heat of formation of the S_N2 transition state is thus not far from that of the products **7** (see dotted lines on Figure 4). The loss of identity of the two molecules of water formally present in complex **13** is consequently not impossible.

Finally, solvation effects upon dehydration of protonated ethanol may be deduced from a comparison between the two sets of calculations discussed in the preceding paragraphs. The solvation energy afforded by one molecule of water may be simply estimated from the data quoted in Tables II and IV as illustrated by Figure 5. Values between 100 to 140 kJ/mol apply for the stable species **1** and **5**, **2** and **6**, and H_3O^+–$H_5O_2^+$; it is reduced to only 42 kJ/mol for the transition state **1**/**2**–**5**/**6**. As shown in Figure 3, transition state **5**/**6** is clearly the water-solvated version of the transition state **1**/**2**. The low value of the solvation energy is in keeping with the large hydrogen-bond length H⋯O (1.875 Å, 6-31G* optimized geometry) between the two molecules of water inside **5**/**6**. Note that the bonding energy of the two molecules of water into $(H_2O)_2$ is comparatively lower (15–24 kJ/mol) with an O⋯H bond length of 2.031 Å (6-31G* calculations).

It may thus be anticipated that the overall critical energy of the acid-catalyzed dehydration via solvated complex **2** is increasingly unfavored as the number of polar solvent molecules increases. This appends a new element to the general observation that proton-catalyzed dehydration of alcohols occurs, in solution chemistry, via an E1 mechanism,[33] avoiding the formation of solvated complexes such as **2**.

Scheme II



III. Dehydration of Protonated Ethanol, Ethanol Cluster

Protonated ROH, ROH clusters have been produced under chemical ionization conditions in a high-pressure source[9,19–21,25,26] or by supersonic expansion.[27] The reactions of protonated alcohol with its neutral precursor were studied by ion cyclotron resonance spectroscopy[10,23] and flowing-afterglow experiments.[24]

In a general manner three reactions were identified:[10,23–29]

(i) a nucleophilic displacement of water

$$ROH_2^+ + ROH \rightarrow RO(H)R^+ + H_2O$$

(ii) a proton transfer

$$ROH_2^+ + ROH \rightarrow ROH + ROH_2^+$$

(iii) acid-catalyzed dehydration

$$ROH_2^+ + ROH \rightarrow R(OH_2)_2^+ + (R-H)$$

For R = CH_3, only the first two reactions may occur and it seems now[24] firmly established that proton transfer (ii) is favored by 1 order of magnitude over methyl transfer (i). From a mechanistic point of view, hydrogen transfer begins by the formation of a proton-bound complex while the methyl transfer begins by the formation of an ion-dipole complex corresponding to a backside nucleophilic attack.[22,30]

For R = C_2H_5, as in the preceding case no dehydration reaction (iii) is observed.[9,23] ICR experiments show that $(C_2D_5OH)_2H^+$ loses specifically a molecule of H_2O; thus, process i occurs without H/D exchanges between carbons and oxygens. However proton transfer between the two hydroxyl groups (ii) is attested and claimed to be fast with respect to (i).[23] This observation is in keeping with the absence of an energy barrier for process ii.

Our results on metastable adducts $(CH_3CD_2OH)_2H^+$ and $(CD_3CH_2OH)_2H^+$ show a facile formation of $CH_3CD_2OH_2^+$ and $CD_3CH_2OH_2^+$ ions, respectively, accompanied by a less intense loss of H_2O (3–5% of the former peaks). These data indicate that reactions i and ii are not preceded by any H/D exchanges between carbons and oxygens in this energy range, as has been also observed under the conditions of the ICR experiments.[23]

The simplest mechanism by which the present data may be explained involves the formation of complexes **14** and **15** (Scheme II). Isomerization **15** → **16** via an S_N2 transition state would lead to the loss of a water molecule.

A potential energy profile may be proposed based on experimental heats of formation and on MO calculations discussed above (Figure 6). Heats of formation of complexes **14**–**17** are estimated from experimental heats of formation of their separated components ($\Delta H_f°(C_2H_5OHC_2H_5)^+$ = 440 kJ/mol,[34] see Tables II and IV for the other species) and from calculated complexation energies. For the latter, it has been assumed that the theoretical data concerning the protonated methanol/methanol system[22] are fully transferable to the protonated ethanol/ethanol case. A complexation energy equal to 50 kJ/mol has been applied to C_2H_4

---

(33) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, Part A, 2nd Ed.; Plenum Press: New York, 1984.

(34) 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.

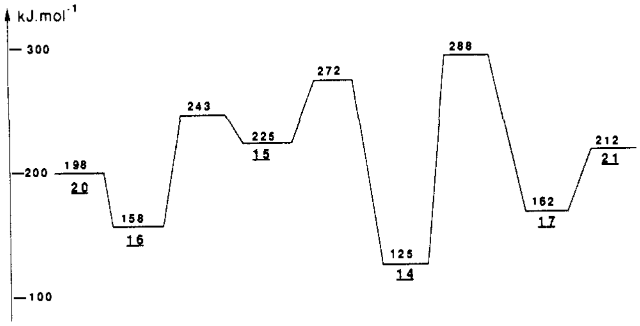
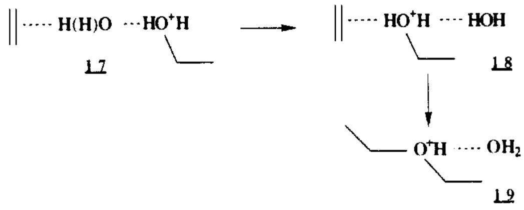


Figure 6. Estimated potential energy profile for the system $C_2H_5OH_2^+$ + C_2H_5OH.

Scheme III



+ **5** → **17**. Transition-state energies have been obtained by using the homologous results presented in Tables III and IV.

As in the case of $(C_2H_5OH, H_2O)H^+$ adducts, the lack of observation of the dehydration products $C_2H_5OH_2\cdots OH_2 + C_2H_4$, despite a favorable thermochemistry ($\Delta H°$ = 212 kJ/mol, experimental value), is probably due to the high energy barrier associated with **14** → **17**. Accordingly, considering the estimations presented in Figure 6, the transition state **14**/**17** should lie in enthalpy near 290 kJ/mol, i.e., only slightly above the products $C_2H_5OH_2^+$ + C_2H_5OH.

In the same vein, the rearrangement **14** → **17** → **18** → **19** (Scheme III), which may also explain the formation of protonated diethyl ether by water loss, is not competitive with **15** → **16**, as attested by the labeling results. This confirms the expectation of a large energy barrier for the process **14** → **17**. Note that, similarly, **18** → **19** should also require a significant amount of energy.

In conclusion, the present study demonstrates that ion-neutral complexes are indeed stable species and may be involved during 1,2 elimination reactions from protonated alcohols. The structure of such complexes is a proton-bound association whose complexation energy, as estimated by high-level molecular orbital calculations, is ca. 70 kJ/mol.

The second important piece of information derived from calculation and experiment is that isomerization of the protonated form into its corresponding proton-bound complex, in the sense of Scheme I, is associated with a high activation energy (greater than 120 kJ/mol). The transition-state energy levels seriously overlap those of the various dissociation products, a phenomenon therfore explaining the subtle balance between hydrogen exchanges and product branching ratios.

Photodissociation of a Bicyclic Azoalkane: Time-Resolved Coherent Anti-Stokes Raman Spectroscopy Studies of Vapor-Phase 2,3-Diazabicyclo[2.2.1]hept-2-ene

J. Stephen Adams,† **R. Bruce Weisman,*** **and Paul S. Engel**

Contribution from the Department of Chemistry and Rice Quantum Institute, Rice University, Houston, Texas 77251.

Received May 29, 1990. Revised Manuscript Received August 3, 1990

Abstract: The photodissociative mechanism of vapor-phase 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) has been studied with nanosecond-regime transient spectroscopic methods. Following excitation of the vibrationless S_1 level at 338.5 nm, data from time-resolved CARS (a vibrational spectroscopy) show the appearance rate for formation of N_2 to be 4×10^7 s^{-1}. This value is significantly slower than the 5×10^8 s^{-1} principal component observed in S_1 fluorescence decay, establishing that the dissociating state is not S_1. CARS measurements on the nascent N_2 photofragments reveal a vibrational distribution (84% v = 0, 12% v = 1) very similar to that observed earlier for the nitrogen formed in the stepwise photodissociation of azomethane. This result and the low level of nascent rotational excitation suggest that dissociation into N_2 plus 1,3-cyclopentanediyl biradical occurs from an excited state of the diazenyl biradical that has a linear CNN bond angle. Transient CARS probing has also revealed the subsequent appearance of bicyclo[2.1.0]pentane formed by ring closure of the 1,3-cyclopentanediyl biradicals. Formation kinetics of this ring closure product shows a single first-order component with a rate coefficient of approximately 5.1×10^6 s^{-1}. This observation implies that S_1 excitation of vapor-phase DBH produces 1,3-cyclopentanediyl biradicals only in their ground triplet state. Mechanistic differences between the gas-phase photochemistries of DBH and acyclic azoalkanes are attributed to a low-lying excited state of the diazenyl biradical that becomes accessible in DBH through the release of ring strain energy.

Introduction

Although the thermal and photochemical dissociation of azoalkanes into nitrogen plus alkyl radicals (RN=NR′ → R + N_2 + R′) has been observed for decades,[1] the mechanisms of these processes generally remain unclear and somewhat controversial.[2] Research in this area centers on determining whether the two C–N bonds break in a single step or in two, identifying and characterizing any reaction intermediates and, in the case of photolysis, understanding the roles played by various electronic states.

Among azoalkanes, the cyclic compounds (those having covalent bonds linking R and R′) command special attention for two reasons. First, the notable differences between their dissociative

---

† Present address: Naval Research Laboratory, Code 6110, Washington, DC 20375.

(1) Ramsperger, H. C. *J. Am. Chem. Soc.* **1927**, *49*, 912.
(2) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.