J. Am. Chem. Soc. **1983**, *105*, 1743-1746

Unusual Low-Energy Isomers of the Ethanol and Dimethyl Ether Radical Cations

Willem J. Bouma, Ross H. Nobes, and Leo Radom*

Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia. *Received July 8, 1982*

Abstract: Ab initio molecular orbital calculations using polarization basis sets and incorporating valence-electron correlation have been used to determine structures and relative energies of isomers in the $C_2H_6O^{+\cdot}$ potential energy surface. In addition to the experimentally well-characterized ethanol and dimethyl ether radical cations, three oxonium ion isomers are reported. These oxonium ions do not have stable, neutral counterparts and therefore cannot be formed experimentally by simple ionization. Remarkably, two of the oxonium ions, $CH_2CH_2OH_2^{+\cdot}$ and $CH_3CHOH_2^{+\cdot}$, are found to lie lower in energy than the ethanol radical cation and, in fact, represent the two lowest energy $C_2H_6O^{+\cdot}$ isomers. The third oxonium ion, $CH_3OHCH_2^{+\cdot}$, is comparable in energy to the dimethyl ether radical cation.

In a theoretical study[1] undertaken some years ago, it was proposed that the radical cation $CH_2CH_2OH_2^{+\cdot}$ (**1**) occurs as an intermediate in reactions catalyzed by adenosylcobalamin (a derivative of vitamin B_{12}), and it was shown that **1** has a substantial binding energy with respect to the fragments $C_2H_4^{+\cdot}$ and H_2O. Renewed interest in this ion has come with its observation in two very recent mass spectrometric studies[2,3] by Terlouw, Holmes, and co-workers. In the first,[2] the technique of collisional activation mass spectrometry was used to demonstrate that **1** is distinct from the well-characterized ethanol and dimethyl ether radical cations (**3** and **5**, respectively), and in a further study,[3] the heat of formation of **1** was measured. A fourth $C_2H_6O^{+\cdot}$ isomer, $CH_3OHCH_2^{+\cdot}$ (**4**), has been reported in a recent theoretical study[4] of the mechanism of fragmentation of $CH_3OCH_3^{+\cdot}$ (**5**); **4** has subsequently been the subject of an experimental study.[3]

In the present study, we have used ab initio molecular orbital calculations to determine the structures and relative energies of **1**, **3**, **4**, **5**, a bridged form (**6**), and the previously unreported $CH_3CHOH_2^{+\cdot}$ (**2**) (see Figure 1). In order to obtain reliable relative energies, polarization basis sets have been used and effects of valence-electron correlation incorporated. We find the remarkable result that the isomers $CH_2CH_2OH_2^{+\cdot}$ (**1**) and $CH_3CHOH_2^{+\cdot}$ (**2**), without stable neutral counterparts, lie lower in energy than the radical cations of ethanol and dimethyl ether.

Method and Results

Standard ab initio molecular orbital calculations have been carried out with a modified version[5a] of the Gaussian 80 system of programs.[5b] Geometries have been determined at the Hartree–Fock (HF) level by using gradient optimization procedures and the 4-31G basis set.[6] Harmonic vibrational frequencies have been calculated at the HF level with the split-valence 3-21G basis[7] at geometries optimized with this basis set. These were used both to characterize stationary points as minima or saddle points (in the HF/3-21G potential energy surface at least) and also to allow calculation of zero-point vibrational energies. More reliable relative energies were obtained from HF calculations using the split-valence 6-31G and split-valence plus dp polarization 6-31G** basis sets,[8,9] and effects of valence-electron correlation have been determined from third-order Møller–Plesset perturbation theory[10] (MP3) calculations with the 6-31G basis set. All calculations on odd-electron species employ the spin-unrestricted formalism.

Our best relative energies are MP3/6-31G** values estimated from eq 1 with the addition of a contribution for zero-point vibrations.

$$\Delta E(\text{MP3}/6\text{-}31\text{G}^{**}) \approx \Delta E(\text{MP3}/6\text{-}31\text{G}) + \Delta E(\text{HF}/6\text{-}31\text{G}^{**}) - \Delta E(\text{HF}/6\text{-}31\text{G}) \quad (1)$$

The additivity approximation (1) has recently been tested and found to hold well.[11] Such estimation schemes are useful when the size of the system precludes direct MP3 calculations with polarization basis sets. Since HF calculations are known[12] to overestimate vibrational frequencies by ~10%, the zero-point vibrational contributions to relative energies have been obtained by scaling the calculated HF/3-21G zero-point energies by a factor of 0.9.

Optimized geometries are displayed within the text. Bond lengths are given in angstroms and bond angles in degrees. Total energies are shown in Table I. The relative energies shown in Table II and referred to in the text are the estimated MP3/6-31G** values with zero-point vibrational contribution.

Comparisons with experimental thermochemical data are based on experimental $\Delta H_{f0}°$ values. In those cases where only $\Delta H_f°_{298}$ values were available in the literature, corrections to 0 K were achieved by using standard formulas[13] and our (scaled) calculated vibrational frequencies.

Discussion

$CH_2CH_2OH_2^{+\cdot}$ (**1**). This ion can be considered as a complex of an ethylene radical cation and a water molecule; the relatively short C–O bond length (1.652 Å) is indicative of a strong association between these fragments. Indeed, the calculated binding

---

[1] (a) Golding, B. T.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1973**, 939. (b) Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 6331.

[2] Terlouw, J. K.; Heerma, W.; Dijkstra, G. *Org. Mass Spectrom.* **1981**, *16*, 326.

[3] Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 2931.

[4] (a) Bouma, W. J.; Nobes, R. H.; Radom, L., presented at the 7th Biennial Conference of the Australian and New Zealand Society for Mass Spectrometry, Sydney, August 1981. (b) Bouma, W. J.; Nobes, R. H.; Radom, L. *Org. Mass Spectrom.* **1982**, *17*, 315.

[5] (a) Farnell, L.; Nobes, R. H., unpublished. (b) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

[6] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

[7] Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

[8] Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

[9] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

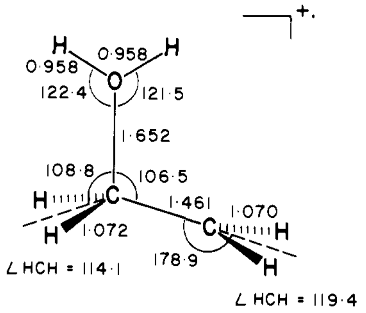
[10] (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

[11] (a) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497. (b) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673.

[12] Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F., Jr.; Hehre, W. J. *Int. J. Quantum Chem., Symp.* **1981**, *15*, 269.

[13] See, for example: (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (b) Stull, D. R.; Westrum, E. F.; Sinke, J. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969. In application of these corrections, no attempt has been made to differentiate torsional from other vibrational modes.

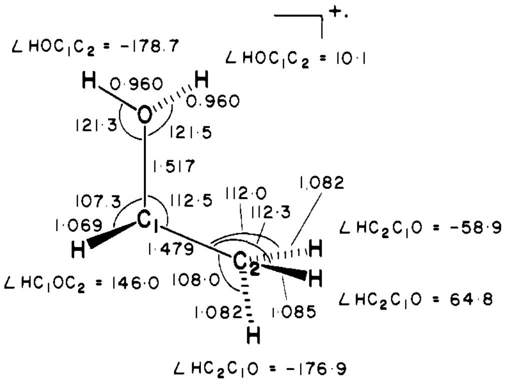
0002-7863/83/1505-1743$01.50/0



1 (C_s)

energy with respect to $C_2H_4^{+\cdot}$ and H_2O is 83 kJ mol^{-1} (Tables I and II); the alternative combination of C_2H_4 and $H_2O^{+\cdot}$ is much higher in energy.[1b,14] We note that **1** is closely related to another ion of unusual structure, $CH_2CH_2OCH_2^{+\cdot}$, a species which was first proposed in a theoretical study[15] and subsequently observed experimentally:[15,16] $CH_2CH_2OCH_2^{+\cdot}$ can be thought of as a complex of an ethylene radical cation and a formaldehyde molecule. The heat of formation of **1** has recently been measured,[3] and a value of 757 kJ mol^{-1} ($\Delta H_f{}^\circ{}_{298}$) obtained.

$CH_3CHOH_2^{+\cdot}$ (**2**). We are unaware of any previous experimental or theoretical studies of $CH_3CHOH_2^{+\cdot}$ (**2**). This ion is calculated to lie 17 kJ mol^{-1} higher in energy than **1**. $CH_3CHOH_2^{+\cdot}$ (**2**) is a homologue of the methylenoxonium ion, $CH_2OH_2^{+\cdot}$, a species which was predicted on the basis of ab initio calculations[17] to be a stable $CH_4O^{+\cdot}$ isomer lying 45 kJ mol^{-1} lower in energy than the methanol radical cation ($CH_3OH^{+\cdot}$). Dissociation of $CH_2OH_2^{+\cdot}$ by loss of an oxygen-bound hydrogen atom was found[17] to have a barrier of 200 kJ mol^{-1}, the endothermicity of this reaction being 108 kJ mol^{-1}. The analogous fragmentation of **2** (yielding the 1-hydroxyethyl cation, $CH_3CHOH^{+\cdot}$), although endothermic by only 37 kJ mol^{-1} (Tables I and II), is also likely to have a large barrier. Experimental observation of $CH_2OH_2^{+\cdot}$ has very recently been reported.[3,18] We might equally expect 2, which lies slightly higher in energy than **1** but lower in energy than the ethanol radical cation (**3**), to be good candidate for experimental observation; this will, however, depend on the barrier to rearrangement to **1**.



2 (C_1)

$CH_3CH_2OH^{+\cdot}$ (**3**). We find two distinct structures for the experimentally well-characterized[19] ethanol radical cation, corresponding roughly to ionization from the C–C or C–O bonds. Lower in energy is **3a**, a structure which resembles a complex of the hydroxymethyl cation (CH_2OH^+) and a methyl radical ($CH_3\cdot$) with a C–C bond length of 2.013 Å. The binding energy of **3a** with respect to CH_2OH^+ and $CH_3\cdot$ is calculated to be 51 kJ mol^{-1} (Tables I and II), which may be compared with a difference of 75 kJ mol^{-1} derived from the results of a photoionization study of ethanol.[20] The long C–C bond length is consistent with the small dissociation energy.[21] The energy of **3a** relative to **1** is calculated to be 43 kJ mol^{-1}, a result which may be compared with an experimental estimate of 21 kJ mol^{-1} based on $\Delta H_{f0}{}^\circ$ values of 772 kJ mol^{-1} for **1** and 793 kJ mol^{-1} for the ethanol radical cation[3,14] (Table II).

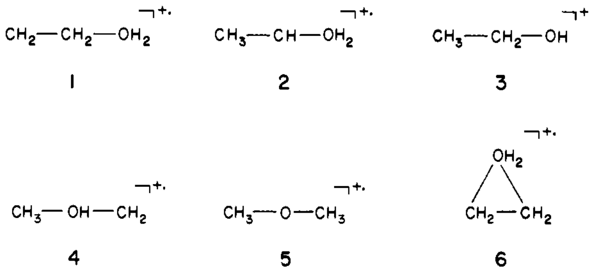
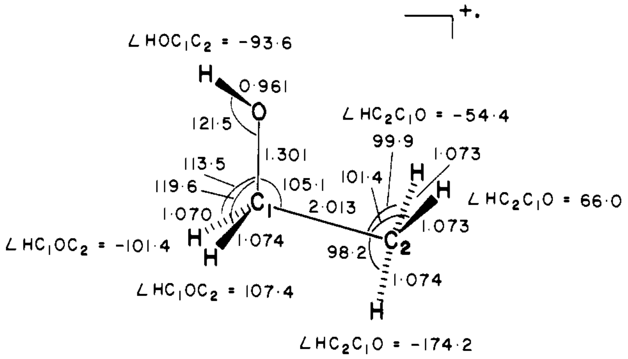
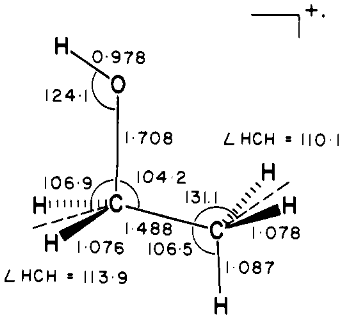


Figure 1. Possible isomeric $C_2H_6O^{+\cdot}$ structures.



3a (C_1)



3b (C_s)

The second structure (**3b**) determined for the ethanol radical cation has a normal C–C bond length (1.488 Å) but an elongated C–O bond (1.708 Å). Due to technical problems, vibrational

---

(14) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl.* **1977**, *6*.

(15) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 2246.

(16) (a) Baumann, B. C.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 7927. (b) Fraser-Monteiro, M. L.; Fraser-Monteiro, L.; Butler, J. J.; Baer, T.; Hass, J. R. *J. Phys. Chem.* **1982**, *86*, 739.

(17) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2929.

(18) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2930.

(19) See, for example: (a) Danchevskaya, M. N.; Tobin, S. N. *Adv. Mass Spectrom.* **1978**, *7*, 1314. (b) Utsunomiya, C.; Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1216.

(20) The value of 75 kJ mol^{-1} is obtained as the difference between the appearance energy (11.25 eV) of CH_2OH^+ and the ionization energy (10.47 eV) of ethanol as reported by Rafaey and Chupka (Refaey, K. M. A.; Chupka, W. A. *J. Chem. Phys.* **1968**, *48*, 5205).

(21) It has been noted in a recent paper on ionized alkanols that the energy required for loss of an alkyl group by carbon–carbon bond cleavage α to the hydroxyl group is small:Holmes, J. L.; Burgers, P. C.; Mollah, Y. A. *Org. Mass Spectrom.* **1982**, *17*, 127. In addition, we have found extreme C–C bond lengthening in alkanes accompanying ionization: Bouma, W. J.; Radom, L. to be published.

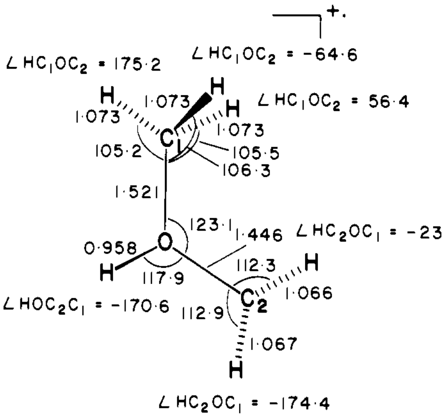
Table I. Calculated Total Energies[a] (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) and Experimental Heats of Formation (kJ mol^{-1}) of $C_2H_6O^{+\cdot}$ Structures and Component Systems

species	symmetry	electronic state	HF/4-31G	HF/6-31G	HF/6-31G**	MP2/6-31G	MP3/6-31G	ZPVE[b]	ΔH_{f0}°
$CH_2CH_2OH_2^{+\cdot}$ (**1**)	C_s	$^2A'$	−153.55223	−153.70905	−153.77291	−153.98365	−154.00329	213.3	772[c]
$CH_3CHOH_2^{+\cdot}$ (**2**)	C_1	^2A	−153.54335	−153.70012	−153.76587	−153.97620	−153.99561	215.0	
$CH_3CH_2OH^{+\cdot}$ (**3a**)	C_1	^2A	−153.50569	−153.66140	−153.74553	−153.94911	−153.96697	214.2	793[d]
$CH_3CH_2OH^{+\cdot}$ (**3b**)	C_s	$^2A''$	−153.52376	−153.67967	−153.74673	−153.93976	−153.96561	*e*	
$CH_3OHCH_2^{+\cdot}$ (**4**)	C_1	^2A	−153.53171[f]	−153.68711[f]	−153.75344	−153.95993	−153.97949[f]	215.6	751[c]
$CH_3OCH_3^{+\cdot}$ (**5**)	C_{2v}	$^2B_1$	−153.53136[f]	−153.68694[f]	−153.75634	−153.95021	−153.97580[f]	216.7	795[d]
$\overline{CH_2CH_2O}H_2^{+\cdot}$ (**6**)	C_{2v}	$^2A_1$	−153.54084	−153.69883	−153.76816	−153.97046	−153.99158	209.3	
$CH_2{=}CH_2^{+\cdot}$	D_{2h}	$^2B_{3u}$	−77.59889	−77.68116	−77.71934	−77.81924	−77.83999	137.8	1075[d]
H_2O	C_{2v}	$^1A_1$	−75.90864	−75.98535	−76.02269	−76.11215	−76.11394	57.2	−239[d]
CH_3CHOH^+	C_s	$^1A'$	−152.99628[g]	−153.15269[g]	−153.23845	−153.44234[g]	−153.45480[g]	190.5	608[d]
$H\cdot$			−0.49823	−0.49823	−0.49823	−0.49823	−0.49823	0.0	216[d]
CH_2OH^+	C_s	$^1A'$	−113.98129[f]	−114.09653[f]	−114.16518	−114.29857	−114.30233[f]	111.8	720[d]
$CH_3\cdot$	D_{3h}	$^2A_2''$	−39.50497[f]	−39.54666[f]	−39.56444	−39.62171	−39.63446[f]	78.1	146[d]

[a] Based on HF/4-31G optimized geometries. [b] HF/3-21G//HF/3-21G values. [c] $\Delta H_f{}^\circ{}_{298}$ values from ref 3, corrected to 0 K by using calculated vibrational frequencies (see text). [d] Reference 14. [e] Not available (see text). [f] Reference 4. [g] From Nobes, R. H.; Rodwell, W. R.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* 1981, *103*, 1913.

frequencies for **3b** could not be calculated, and **3b** was therefore established to be a minimum by examining distorted structures in the vicinity of the optimized structure. In order to obtain a relative energy at the same level as for the other isomers, we have assumed the zero-point vibrational energy of **3b** to be the same as that of **3a**. Our best calculations then indicate that **3b** lies 48 kJ mol^{-1} above **3a**.

$CH_3OHCH_2^{+\cdot}$ (4). In a recent theoretical study[4] of the nature of the COH_3^+ ion produced in the mass spectrometer from precursors such as dimethyl ether, it was postulated that, prior to fragmentation to give CH_2OH^+ and $CH_3\cdot$, a 1,2-hydrogen shift in the dimethyl ether radical cation (**5**) will yield as an intermediate the oxonium ion $CH_3OHCH_2^{+\cdot}$ (**4**). Structure **4** is related to a recently identified[22] $C_3H_8O^{+\cdot}$ isomer, $CH_3OHCH_2CH_2^{+\cdot}$, as well as to the methylenoxonium ion, $CH_2OH_2^{+\cdot}$. Our calculations indicate that 4, lying 59 kJ mol^{-1} above **1**, is comparable in energy to the dimethyl ether radical cation (**5**). In contrast, a recently reported[3] $\Delta H_f{}^\circ{}_{298}$ for **4** of 736 kJ mol^{-1} leads to a ΔH_{f0}° of 751 kJ mol^{-1}, i.e., an energy lower than that of all the other $C_2H_6O^{+\cdot}$ isomers. The discrepancy between theory and experiment is sufficiently large here that we would suggest a reexamination of the experimental data. It is possible, for example, that **1** rather than **4** was observed in the experimental study.



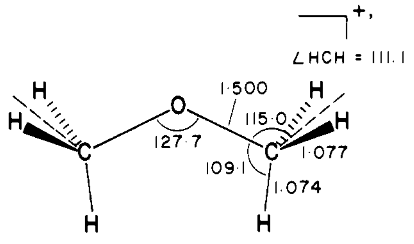
4 (C_1)

$CH_3OCH_3^{+\cdot}$ (5). The dimethyl ether radical cation (**5**) is experimentally well characterized.[23] Recently, the ESR spectrum of **5** was reported,[24] and its heat of formation (795 kJ mol^{-1}) is well established.[14] The most stable structure of **5** is found to possess C_{2v} symmetry but, in contrast to neutral dimethyl ether, has both methyl groups *eclipsing* rather than staggering the neighboring C–O bonds. The energy difference between **5** and **1** is calculated to be 61 kJ mol^{-1}, considerably larger than the experimental difference (23 kJ mol^{-1}). We note that in a previous theoretical study[4] the barrier to rearrangement of **5** to **4** was found to be substantial (146 kJ mol^{-1}).

Table II. Calculated and Experimental Relative Energies (kJ mol^{-1}) of $C_2H_6O^{+\cdot}$ Structures and Component Systems

	calcd[a]	exptl[b]
$CH_2CH_2OH_2^{+\cdot}$ (**1**)	0	772
$CH_3CHOH_2^{+\cdot}$ (**2**)	17	
$CH_3CH_2OH^{+\cdot}$ (**3a**)	43	793
$CH_3CH_2OH^{+\cdot}$ (**3b**)	91[c]	
$CH_3OHCH_2^{+\cdot}$ (**4**)	59	751
$CH_3OCH_3^{+\cdot}$ (**5**)	61	795
$\overline{CH_2CH_2O}H_2^{+\cdot}$ (**6**)	13	
$CH_2{=}CH_2^{+\cdot}$ + H_2O	83	836
CH_3CHOH^+ + $H\cdot$	54	824
CH_2OH^+ + $CH_3\cdot$	94	866

[a] MP3/6-31G** values estimated from eq 1 with zero-point vibrational contribution (see text). [b] Based on H_{f0}° values of Table I. [c] Assuming that the zero-point vibrational energy of **3b** is the same as that of **3a** (see text).



5 (C_{2v})

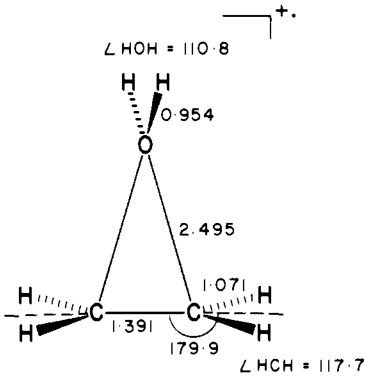
Bridged $\overline{CH_2CH_2O}H_2^{+\cdot}$ (6). The final structure considered is bridged $\overline{CH_2CH_2O}H_2^{+\cdot}$ (**6**). This structure is found not to be a minimum in the HF/4-31G potential energy surface. Indeed, the HF/3-21G//HF/3-21G frequency calculations indicate that **6** has one imaginary frequency, and thus in the HF/3-21G surface at least **6** represents the transition structure for the degenerate 1,2-OH_2 shift in **1**. A similar result has been reported previously

---

(22) Crow, F. W.; Gross, M. L.; Bursey, M. M. *Org. Mass Spectrom.* **1981**, *16*, 309.

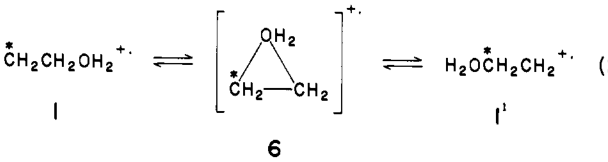
(23) See, for example: Aue, D. H.; Webb, H. M.; Davidson, W. R.; Vidal, M.; Bowers, M. T.; Goldwhite, H.; Vortal, L. E.; Douglas, J. E.; Kollman, P. A.; Kenyon, G. L. *J. Am. Chem. Soc.* **1980**, *102*, 5151.

(24) Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1981**, *103*, 6994.



6 (C_{2v})

for the CHCHOH$_2^{+\cdot}$ system.[25] It is well established[26] that both inclusion of polarization functions and of electron correlation stabilize such nonclassical cations with respect to classical structures. Nevertheless, our best calculations (Tables I and II) indicate that the open form **1** is favored slightly (by 13 kJ mol^{-1}) over the bridged species **6**. In view of this result, we would predict that scrambling of the CH$_2$ groups in **1** (eq 2) should occur readily under normal experimental conditions.



(2)

Conclusions

The present study substantiates the recently reported observation[3] of CH$_2$CH$_2$OH$_2^{+\cdot}$ (**1**) as a low-energy isomer in the C$_2$H$_6$O$^{+\cdot}$ potential energy surface. This ion is calculated to be lower in energy than both the ethanol and dimethyl ether radical cations (by 43 and 61 kJ mol^{-1}, respectively). Two other ions, unusual in that they too have no stable neutral counterparts, are also shown to be low in energy: CH$_3$CHOH$_2^{+\cdot}$ (**2**) lies 26 kJ mol^{-1} below the ethanol radical cation, and CH$_3$OHCH$_2^{+\cdot}$ (**4**) is comparable in energy to the dimethyl ether radical cation. Both **2** and **4** offer good prospects for experimental observation. All three oxonium ion structures (**1**, **2**, and **4**) are members of a class of radical cations which can be considered as complexes of a radical cation (e.g., CH$_2^{+\cdot}$, CHCH$^{+\cdot}$, CH$_2$CH$_2^{+\cdot}$, CH$_3$CH$^{+\cdot}$) and an electron-rich neutral molecule (e.g., H$_2$O, NH$_3$, HF, HCl, CH$_3$OH, CH$_2$=O). Many such complexes have recently been theoretically and/or experimentally identified.[1-4,15-18,22,25,27] Finally, we note that the transition structure (**6**) for 1,2-OH$_2$ migration in CH$_2$CH$_2$OH$_2^{+\cdot}$ (**1**) is found to lie only 13 kJ mol^{-1} higher in energy than **1**, suggesting that scrambling of the carbon atoms in suitably labeled **1** should occur readily.

Acknowledgment. We thank Dr L. Farnell for the vibrational frequency program. Helpful discussions with Dr J. K. MacLeod are gratefully acknowledged.

Registry No. 1, 60786-90-5; **2**, 84602-72-2; **3**, 84602-73-3; **4**, 84602-74-4; **5**, 79802-70-3.

---

(25) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1979**, *101*, 5540.

(26) See, for example: Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(27) See also: (a) Lathan, W. A.; Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *11*, 175. (b) Corderman, R. R.; LeBreton, P. R.; Buttrill, S. E.; Williamson, A. D.; Beauchamp, J. L. *J. Chem. Phys.* **1976**, *65*, 4929. (c) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724. (d) Van Velzen, P. N. T.; Van Der Hart, W. J. *Chem. Phys. Lett.* **1981**, *83*, 55. (e) Bouma, W. J.; Dawes, J. M.; Radom, L. *Org. Mass Spectrom.* **1983**, *18*, 12. (f) Bouma, W. J.; Yates, B. F.; Radom, L. *Chem. Phys. Lett.* **1982**, *92*, 620. (g) Halim, H.; Ciommer, B.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 528. (h) Frisch, M. J.; Raghavachari, K.; Pople, J. A.; Bouma, W. J.; Radom, L. *Chem. Phys.*, in press.

Theoretical Aspects of the Photochemistry of Methanol, Methylamine, and Related Materials

E. Kassab,*[†] J. T. Gleghorn,[‡] and E. M. Evleth[†]

Contribution from the Centre de Mécanique Ondulatoire Appliquée, 23, rue du Maroc, 75019, Paris, France, and the Department of Chemistry, University of Lancaster, Lancaster, United Kingdom. *Received April 23, 1982*

Abstract: The photochemistries of methanol and methylamine are computationally rationalized using ab initio methods. It is shown that the lowest excited singlet states of these and related materials are n,3s Rydberg in character. These states are computationally shown to evolve adiabatically to the valence ground states of the various radical products along the NH, CN, CO, and OH bond rupture pathways in methylamine and methanol, respectively. The NH and CN n,3s bond rupture surfaces display minima in the region of the Franck–Condon excitation geometry. The NH bond ruptures in n,3s singlet ammonia and methylamine are shown to be identical in having small activation energies. The CN excited state bond rupture shows a much larger activation energy, indicating that trialkylamines should display some photostability in the region of the 0–0 transition. In methanol, neither CO nor OH excited-state bond rupture coordinates show minima. The observed preference for OH bond rupture in the UV photochemistry of methanol is rationalized as resulting from the lighter mass of the H atom as well as the computed more repulsive nature of the OH bond rupture. In methanol, both 1,2- and 1,1-H$_2$ molecular elimination excited-state pathways are examined. 1,2-H$_2$ elimination is found to have a small activation energy while the 1,1-elimination is difficult. The concept of de-Rydbergization is fully developed in order to rationalize the change in electronic character occurring along these various excited state pathways.

The goal of this article is to characterize theoretically the absorption threshold photochemistry of methanol, methylamine, and related small molecules. We will show that the excited states generated in the absorption threshold region are all singlet and Rydberg (n,3s) in character. We will also show that there are adiabatic surfaces which allow these Rydberg states to evolve directly to the valence states of the fragmentation products.

Previous emphasis on the properties of small-molecule excited states has been largely spectroscopic.[1] Standard photochemical

---

[†] Centre de Mécanique Ondulatoire Appliquée.

[‡] University of Lancaster.

0002-7863/83/1505-1746$01.50/0