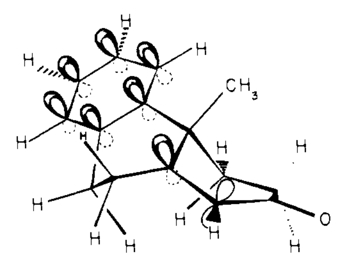
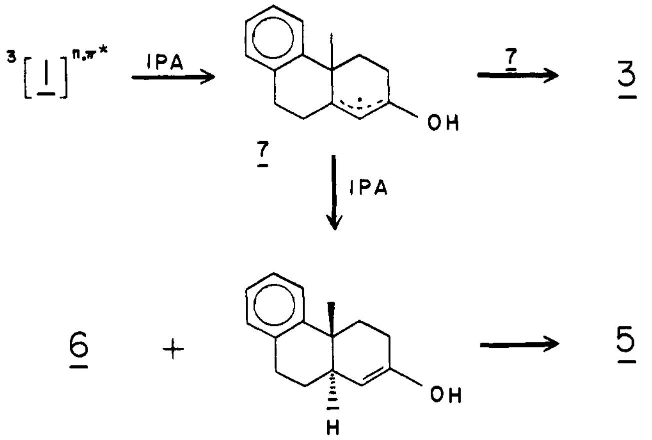


Figure 2. Phenanthrone **1** in its relaxed $^3\pi,\pi^*$ state.

Scheme II



that reduction of the C=C bond of **1** occurs by different mechanisms with opposite stereochemistry from two distinct triplet excited states is unprecedented. The possible generality of this phenomenon will be examined in other enones where the substitution pattern permits elucidation of the stereochemical course of this transformation.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant CHE-7819750.

Registry No. 1, 6606-34-4; **2**, 6606-35-5; **3**, 7363-88-4; **4**, 70524-91-3; **5**, 1686-50-6; **6**, 81457-34-3.

The Methylenoxonium Radical Cation ($CH_2OH_2^{+}\cdot$): A Surprisingly Stable Isomer of the Methanol Radical Cation

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

Research School of Chemistry
Australian National University
Canberra, ACT 2600, Australia

Received October 28, 1981

The simplest alcohol, methanol (CH_3OH), is the only low-energy isomer in the CH_4O potential-energy surface.[1] This has also generally been assumed to be the case for the radical cation, most experimental studies of the $CH_4O^{+}\cdot$ system to date having been discussed in terms of the $CH_3OH^{+}\cdot$ structure (**1**).[2] We report in this communication a second $CH_4O^{+}\cdot$ structure, the methylenoxonium radical cation $CH_2OH_2^{+}\cdot$ (**2**), that not only represents an additional stable isomer in the $CH_4O^{+}\cdot$ potential-energy surface but lies lower in energy than $CH_3OH^{+}\cdot$ itself.

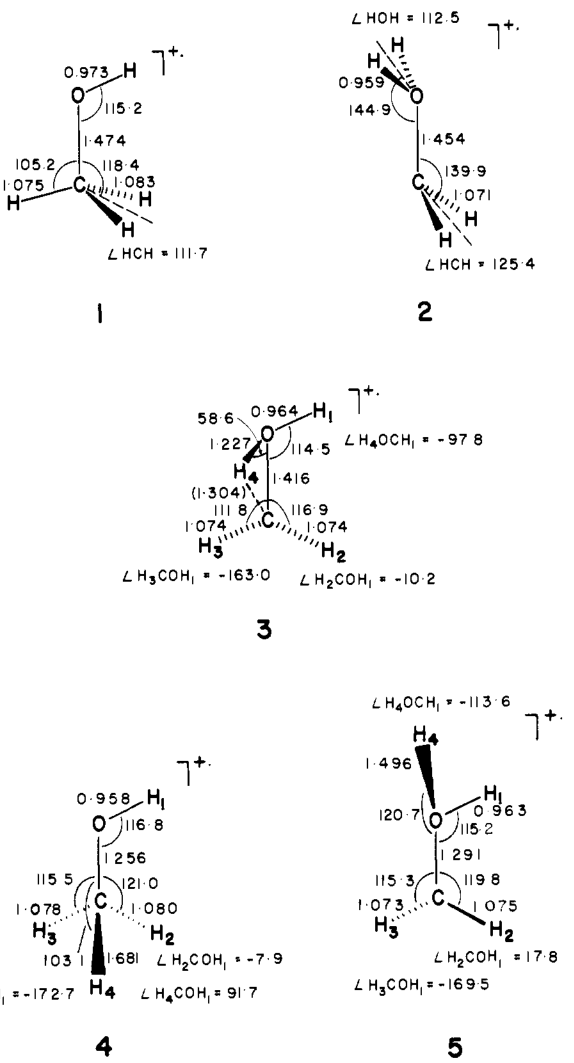


Figure 1. Optimized geometries (HF/6-31G**) of $CH_4O^{+}\cdot$ isomers (**1** and **2**) and transition structures (**3**–**5**).

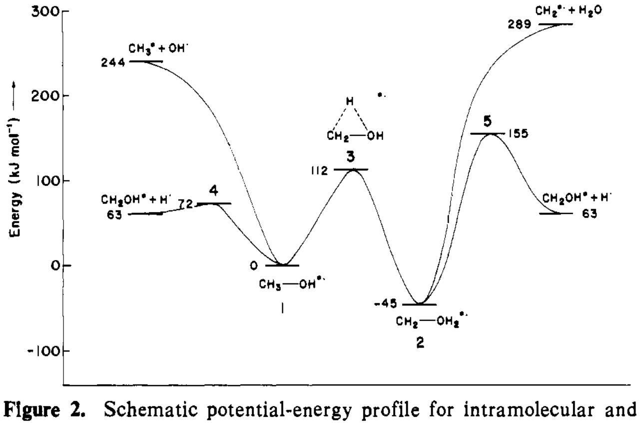


Figure 2. Schematic potential-energy profile for intramolecular and dissociative rearrangements in the $CH_4O^{+}\cdot$ system.

Ab initio molecular orbital calculations with a large basis set and incorporating electron correlation were carried out[3] for **1**, **2**, the transition structure **3** separating these isomers, the transition structures **4** and **5** for loss of H· from **1** and **2**, respectively, and for the dissociation products CH_2OH^{+} + H·, CH_3^{+} + OH·, and $CH_2^{+}\cdot$ + H_2O. Geometry optimizations utilized analytical gra-

---

[1] Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394.

[2] See, for example (a) Beynon, J. H.; Fontaine, A. E.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1*, 1. (b) Bertrand, M.; Beynon, J. H.; Cooks, R. G. *Ibid.* **1972**, *9*, 346. (c) Bertrand, M.; Beynon, J. H.; Cooks, R. G. *Org. Mass Spectrom.* **1973**, *7*, 193. (d) Cooks, R. G.; Hendricks, L.; Beynon, J. H. *Ibid.* **1975**, *10*, 625.

[3] With a modified version[4] of the GAUSSIAN 80 system of programs: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; De Frees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

[4] Farnell, L.; Nobes, R. H., unpublished material.

Table I. Calculated Relative Energies[a] and Zero-Point Vibrational Energies[b] (ZPVE) (kJ mol^{-1}) for $CH_4O^{+\cdot}$ Ions and Fragments

	MP3/ 6-31G**	ZPVE	MP3/ 6-31G** (including ZPVE)[c]
$CH_3OH^{+\cdot}$ **1**	0	133.9[d]	0
$CH_2OH_2^{+\cdot}$ **2**	−49.7	139.4	−44.7
TS **3**	118.2	126.7	111.8
TS **4**	83.1	121.7	72.1
TS **5**	167.0	120.2	154.7
$CH_2OH^+ + H\cdot$	79.9	114.6	62.6
$CH_3^+ + OH\cdot$	264.8	111.1	244.4
$CH_2^{+\cdot} + H_2O$	312.9	105.9	287.7

[a] For HF/6-31G** optimized structures; MP3/6-31G**//HF/6-31G** total energy for $CH_3OH^{+\cdot}$ is −115.009 26 hartrees. [b] Determined at the HF/4-31G//HF/6-31G** level. [c] Obtained by including zero-point vibrational energies scaled to 90%: Pople, J. A.; Schlegel, H. B.; Krishnan, R.; De Frees, D. J.; Binkley, J. S., Frisch, M. J.; Whiteside, R. A.; Hout, Jr, R. F.; Hehre, W. J. *Int. J. Quantum Chem.*, in press. [d] From the HF/4-31G optimized structure of eclipsed 1.

dient techniques with the split-valence plus *dp* polarization 6-31G** basis set.[5] Characterization of stationary points (as minima or saddle points) was confirmed through calculation of harmonic vibrational frequencies. These were also used to evaluate zero-point vibrational energies. Finally, calculations incorporating valence-electron correlation at the third-order Møller–Plesset (MP3) level[6] were carried out with the 6-31G** basis set to enable improved energy comparisons.[7] The use of Hartree–Fock (as opposed to correlated) geometries was shown to be a very reasonable approximation in the neutral methanol study of Pople et al.[1] All calculations on odd-electron species utilized the spin-unrestricted formalism. Calculated energies are presented in Table I, structures are given in Figure 1, and a schematic energy profile for the rearrangement and various dissociative processes in the $CH_4O^{+\cdot}$ surface is displayed in Figure 2.

In contrast to the situation in the neutral CH_4O surface where the structure $CH_2 \cdots OH_2$ represents a weak complex[1,8] with a long C···O bond (1.805 Å with MP2/6-31G*),[1] $CH_2OH_2^{+\cdot}$ (**2**) is a tightly bound species with a C–O length (1.454 Å, Figure 1) even shorter than the C–O length (1.474 Å) in $CH_3OH^{+\cdot}$ (**1**).

Again, whereas $CH_2 \cdots OH_2$ lies in a shallow potential well, high (354 kJ mol^{-1})[1] above CH_3OH, $CH_2OH_2^{+\cdot}$ lies in a deep potential well 45 kJ mol^{-1} *lower* than that of $CH_3OH^{+\cdot}$ (Table I). Thus $CH_2OH_2^{+\cdot}$ is the most stable $CH_4O^{+\cdot}$ isomer and should certainly be experimentally observable. Indeed, $CH_2OH_2^{+\cdot}$ *has* been detected in solution by ESR spectroscopy.[9] However, no gas-phase observation of this species has yet been reported.

Rearrangement and dissociative processes in the $CH_4O^{+\cdot}$ system have also been examined. The 1,2 hydrogen shift converting $CH_3OH^{+\cdot}$ (**1**) to $CH_2OH_2^{+\cdot}$ (**2**) via transition structure **3** is found to require 112 kJ mol^{-1}. This is 40 kJ mol^{-1} more than is required for hydrogen atom loss from **1** (via **4**), and such a process would therefore not represent a viable means of production of $CH_2OH_2^{+\cdot}$. It is interesting to note that loss of a carbon-bound hydrogen atom from **1** (via **4**) is accompanied by only a small reverse activation energy (9 kJ mol^{-1}), whereas loss of an oxygen-bound hydrogen atom from **2** (via **5**) has considerable reverse activation energy (92 kJ mol^{-1}). Dissociations involving C–O bond cleavage (**1** → methyl cation + hydroxyl radical, **2** → methylene radical cation + water) are found to be higher energy processes and to have zero reverse activation energy.

Although early experimental studies found specific loss[2] of a methyl hydrogen from $CH_3OH^{+\cdot}$ (to give CH_2OH^+), recent photoionization studies[10,11] of the fragmentation of $CH_3OH^{+\cdot}$ have shown that at threshold energies, scrambling of the hydrogen atoms in $CD_3OH^{+\cdot}$ is observed to a minor extent (~5%). Interconversion of **1** and **2** via a 1,2 hydrogen shift (Figure 2) offers a suitable mechanism for hydrogen scrambling in $CD_3OH^{+\cdot}$. It appears that this interconversion can occur to a small extent prior to the loss of H· from **1**. The scrambling reported[10] at higher energies for the dissociation of $CH_3OH^{+\cdot}$ to $CH_2^{+\cdot}$ and H_2O is not surprising since interconversion of $CH_3OH^{+\cdot}$ (**1**) and $CH_2OH_2^{+\cdot}$ (**2**) requires substantially less energy than does this dissociation process.

Since production of **2** from initially formed **1** is not an efficient process, alternative pathways for its generation in the gas-phase need to be devised and tested. Experiments in this direction are well advanced.[12]

Acknowledgment. Useful discussions with Dr. J. K. MacLeod are gratefully acknowledged.

Registry No. 1, 12538-91-9; **2**, 25765-84-8; **3**, 17836-08-7.

---

(5) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, *28*, 213.

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

(7) Calculations at this level are denoted MP3/6-31G**//HF/6-31G**, which means an energy calculation at the MP3 level with the 6-31G** basis set using a geometry optimized at the Hartree–Fock level with the 6-31G** basis set.

(8) Eades, R. A.; Gassman, P. G.; Dixon, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 1066.

(9) Brimage, D. R. G.; Cassell, J. D. P.; Sharp, J. H.; Symons, M. C. R. *J. Chem. Soc. A* **1969**, 2619.

(10) Berkowitz, J. *J. Chem. Phys.* **1978**, *69*, 3044.

(11) Momigny, J.; Wankenne, H.; Krier, C. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *35*, 151.

(12) **Note Added in Proof:** These experiments have now been successfully completed: Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* following paper in this issue. Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.*, this issue.

Experimental Evidence for the Existence of a Stable Isomer of $CH_3OH^{+\cdot}$: The Methylenoxonium Radical Cation, $CH_2OH_2^{+\cdot}$

Willem J. Bouma, John K. MacLeod,* and Leo Radom

Research School of Chemistry
Australian National University
Canberra, ACT 2600, Australia

Received November 30, 1981

Recent ab initio molecular orbital calculations[1] have predicted the existence of a hitherto unreported and unexpected isomer of the methanol radical cation, $CH_3O^{+\cdot}$ (**1**). The new isomer, methylenoxonium, $CH_2OH^{+\cdot}$ (**2**), was found to be lower in energy than the well-known **1** by 45 kJ mol^{-1}. In this communication we report experimental verification of the prediction that **2** is a stable, observable gas-phase species.

As the target ion **2** has no known neutral counterpart (CH_2OH_2 is calculated to be very high in energy[2]), the mode of generation requires special consideration. Our strategy was to generate **2** as the product ion in a mass spectrometric rearrangement/fragmentation reaction, characterized by an intramolecular hydrogen shift in the rearrangement stage and the expulsion of a stable, neutral moiety in the fragmentation. Such rearrangement/fragmentation reactions appear to offer a good general approach for the generation of ions whose neutral counterparts are either unknown[3a,4b] or difficult to generate.[5] For our present purposes,

---

(1) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.*, in press.

(2) Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394.

(3) (a) Terlouw, J. K.; Heerma, W.; Dijkstra, G. *Org. Mass. Spectrom.* **1981**, *16*, 326. (b) Holmes, J. L., presented at the 7th Biennial Conference of the Australian and New Zealand Society for Mass Spectrometry, Sydney, August 1981.

(4) (a) Busch, K. L.; Nixon, W. B.; Bursey, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 1621. (b) Crow, F. W.; Gross, M. L.; Bursey, M. M. *Org. Mass. Spectrom.* **1981**, *16*, 309.