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.

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(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, $CH_2OH_2^{+\cdot}$

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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,

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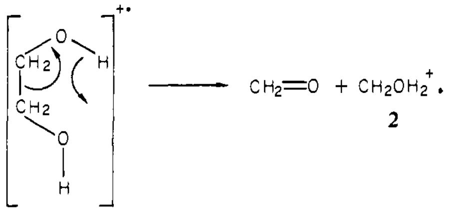
Table I. Collisional Activation Spectra (m/z) for $CH_4O^{+\cdot}$ Isomers Obtained by a B/E Scan[a,b]

	12	13	14	15	16	17	18	19
1, $CH_3OH^{+\cdot}$	10	20	27	26	5[c]	8[c]	4[c]	1
$CD_3OH^{+\cdot}$	4		9		23	2	59	2
2, $CH_2OH_2^{+\cdot}$	13	25	32	3	8[c]	6[c]	10[c]	2
$CD_2OH_2^{+\cdot}$ [d]	12		29	2	44	7	4	3

[a] Recorded at 70 eV on a VG Micromass 7070 mass spectrometer, using helium as collision gas to give 50% reduction of the m/z 32 ion current. No change in the CA spectra was observed for 75% reduction; the spectra did not change significantly when recorded at lower ionizing energies (20 eV). None of the tabulated ions were present in the unimolecular metastable spectra. Abundances are normalized to 100 for the peak group m/z 12-19. Values quoted are an average of several scans. [b] The origin of the fragment ions was verified by localized V scans and by B^2/E scans: Lacey, M. J.; MacDonald, C. G. *Org. Mass Spectrom.* 1979, *14*, 465; 1980, *15*, 134. [c] Oxygen-containing ions, $O^{+\cdot}$, OH^+, and $OH_2^{+\cdot}$, were included because of their possible overlap with deuterated hydrocarbon ions. [d] Generated from $HOCD_2CD_2OH$.

we chose ethylene glycol as a suitable progenitor ion, which might be expected to yield **2** after loss of a formaldehyde molecule (eq 1).[6]



2

(1)

By use of a conventional double-focusing (EB geometry) mass spectrometer, equipped with a collision chamber, together with a B/E-linked scan,[7a] collisional activation (CA) spectra[7b] were obtained on the ions of m/z 32 ($CH_4O^{+\cdot}$) produced from methanol and ethylene glycol. *The spectra clearly demonstrate that these isomeric ions have different structures.* The fragment ions in the CH_n peak group, m/z 12-15, of the unlabeled compounds were analyzed, and the results are summarized in Table I. In the CA spectrum of the ion **1** from methanol, fragment ions $C^{+\cdot}$, CH^+, $CH_2^{+\cdot}$, and CH_3^+ were observed, while for the ion from ethylene glycol the CH_3^+ ion (m/z 15) was virtually absent, as would be expected from our proposed structure ($CH_2OH_2^{+\cdot}$) for this ion. The CA spectra of $CD_3OH^{+\cdot}$ and $CD_2OH_2^{+\cdot}$ (the latter formed from $HOCD_2CD_2OH$ as expected from reaction 1) show that little or no interconversion of **1** and **2** occurs. Thus, in both cases, the CH^+ and $CH_2^{+\cdot}$ fragment ions have shifted almost exclusively to CD^+ (m/z 14) and $CD_2^{+\cdot}$ (m/z 16) (Table I) with virtually no CH^+, $CHD^{+\cdot}$, or $CHD_2^{+\cdot}$ being detected.

It is worth noting that the $CH_2OH_2^{+\cdot}$ isomer is one of the simplest members of a new "class" of radical cations, which have been shown theoretically to correspond to a strong association of a radical cation (in this case $CH_2^{+\cdot}$) with a neutral molecule (in this case H_2O). Other members of this class that have recently been experimentally identified or theoretically predicted include $CH_2{-}O{=}CH_2^{+\cdot}$,[8,9] $CH_2CH_2{-}O{=}CH_2^{+\cdot}$,[10] $CH_3CH{-}O{=}CH_2^{+\cdot}$,[10a] $CHCH{-}OH_2^{+\cdot}$,[9b] $CH_2CH_2{-}OH_2^{+\cdot}$,[3] $CH_2{-}OHCH_3^{+\cdot}$,[11] and $CH_2CH_2{-}OHCH_3^{+\cdot}$.[4] Such ions can characteristically transfer the radical cation moiety to other neutral molecules such as nitriles,[4a,9a,10] a process that bears some analogy to solvent exchange.

Registry No. $CH_3OH^{+\cdot}$, 12538-91-9; $CD_3OH^{+\cdot}$, 81256-31-7; $CH_2OH_2^{+\cdot}$, 25765-84-8; $CD_2OH_2^{+\cdot}$, 81256-32-8.

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The Radical Cation $[CH_2OH_2]^{+\cdot}$ and Related Stable Gas-Phase Ion-Dipole Complexes

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Ab initio molecular orbital theory calculations[1] have predicted that the ion-dipole complexes $[CH_2CH_2OH_2]^{+\cdot}$ (**1**) and $[CH_2CH_2NH_3]^{+\cdot}$ may exist as stable species in the gas phase. In 1981 the existence of the radical cation $[CH_3OHCH_2CH_2]^{+\cdot}$ (**2**) was inferred by Crow et al.[2] from observations of the collisional activation[3] (CA) mass spectrum of the ion $[C_3H_8O]^{+\cdot}$, m/z 60, generated from ionized 1,2-dimethoxyethane by loss of CH_2O. Simultaneously Terlouw et al.[4] concluded that **1** resulted from loss of CH_2O from ionized 1,3-propanediol; **1** was characterized by its CA mass spectrum, which differed markedly from those of its isomers $[CH_3CH_2OH]^{+\cdot}$ and $[CH_3OCH_3]^{+\cdot}$, and by an intense Gaussian-type metastable peak for H_2O loss, a process absent in the mass spectra of the latter two compounds. We report briefly here the identification of seven complexes, $[CH_2XH]^{+\cdot}$, X = OH, NH_2, SH, Cl, Br, the complex $[CHClClH]^{+\cdot}$ and $[CH_2HOCH_3]^{+\cdot}$. We have also measured heats of formation, ΔH_f, of some complexes. The first new complex $[CH_2OH_2]^{+\cdot}$ (**3**) has been the subject of very recent ab initio calculations,[5] and its existence was confirmed by a CA mass spectrum.[6] We have generated **3** by the dissociative ionizations of $HOCH_2CH_2OH$, $HOCH_2CHO$, and $HOCH_2COOH$, by loss of CH_2O, CO, and CO_2, respectively, from their molecular ions. The CA mass spectrum (ZAB-2F mass spectrometer) of $[CH_4O]^{+\cdot}$ generated from $HOCH_2CH_2OH$, is shown in Figure 1 together with that of ionized methanol. Differences between the CA spectra are striking and clearly are characteristic of the ion structures. Note too, the intense, narrow m/z 16 peak $[CH_4O]^{2+}$ in the spectrum of **3**, showing that a significant binding energy must exist between $[CH_2]^{+\cdot}$ and $[H_2O]^{+\cdot}$ and that the doubly charged complex is inaccessible from ionized methanol. The stability of $[CH_2{\cdot}H_2]^{2+}$ and its generation by charge stripping from $[CH_4]^{+\cdot}$ (and *not* directly from CH_4 by high-energy electron or photon impact) has been of recent interest.[7]

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