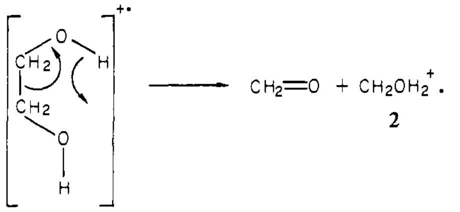
Table I. Collisional Activation Spectra (m/z) for $CH_4O^{+\cdot}$ Isomers Obtained by a B/E Scan[a,b]

	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]



(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.

---

(5) McLafferty, F. W.; McAdoo, D. J.; Smith, J. S.; Kornfield, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 3720.

(6) The relative abundance of the m/z 32 ion in the mass spectrum of ethylene glycol is about 10% RI.

(7) (a) Stradling, R. S.; Jennings, K. R.; Evans, S. *Org. Mass Spectrom.* **1978**, *13*, 429. (b) For a recent review, see: McLafferty, F. W. *Acc. Chem. Res.* **1980**, *13*, 33 and references therein.

(8) Corderman, R. R.; LeBreton, P. R.; Buttrill, S. E.; Williamson, A. D.; Beauchamp, J. L. *J. Chem. Phys.* **1976**, *65*, 4929.

(9) (a) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724. (b) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1979**, *101*, 5540.

(10) (a) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 2246. (b) Baumann, B. C.; MacLeod, J. K.; Radom, L. *Ibid.* **1980**, *102*, 7927.

(11) (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.*, in press.

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

J. L. Holmes* and F. P. Lossing

Department of Chemistry, University of Ottawa
Ottawa, Ontario, K1N 9B4 Canada

J. K. Terlouw and P. C. Burgers

Analytical Chemistry Laboratory, University of Utrecht
Utrecht 35AD, The Netherlands

Received January 11, 1982

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]

---

(1) Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 6331.

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

(3) McLafferty, F. W. In "High Performance Mass Spectrometry: Chemical Applications"; Gross, M. L., Ed.; American Chemical Society: Washington, D.C., 1978; ACS Symp. Ser. No. 70, 47.

(4) Terlouw, J. K.; Heerma, W.; Dijkstra, G. *Org. Mass Spectrom.* **1981**, *16*, 326.

(5) Bouma, W. J.; Nobes, R. H.; Radom, L., submitted for publication.

(6) McLeod, J. K.; Bouma, W. J.; Radom, L., submitted for publication.

(7) Ast, T.; Porter, C.; Proctor, C. J.; Beynon, J. H. *Chem. Phys. Lett.* **1981**, *78*, 439. Hanner, A. W.; Moran, T. F. *Org. Mass Spectrom.* **1981**, *16*, 512.

0002-7863/82/1504-2931$01.25/0

Table I. Charge-Stripping Mass Spectra[a] of $[CH_3X]^{+\cdot}$ and $[CH_2XH]^{+\cdot}$ Ions

	conventional isomer[b]				$[CH_2XH]^{2+}$ species			
X	CH_3X^{2+}	CH_2X^{2+}	CHX^{2+}	precursor molecule	neutral fragment	CXH_3^{2+}	CXH_2^{2+}	CXH^{2+}
OH	~0	~80	~20	$HOCH_2CH_2OH$	CH_2O	95	5	<1
NH_2	20	30	50	$HOCH_2CH_2NH_2$	CH_2O	94	6	<1
SH	40	40	20	$HOCH_2CH_2SH$	CH_2O	50	25	25
Cl	10	40	50	$CH_2ClCOOH$	CO_2	85	10	5
Br	<10	45	45	$CH_2BrCOOH$	CO_2	70	15	15
Cl_2	<10[c]	80[c]	<10[c]	$CHCl_2COOH$	CO_2	95[d]	3[d]	3[d]

[a] Measured as described in ref 13. Abundances normalized to 100 units. It should be noted that the absolute intensities of doubly charged ions are very weak for $[CH_3X]^{2+}$ ions, and thus all data for these species are approximate values only. [b] Doubly charged ions from collisional ionization of $CH_3X^{+\cdot}$ ions generated by electron impact on CH_3X molecules. [c] Derived from $[CH_2Cl_2]^{+\cdot}$. [d] Derived from $[CHCl_2COOH]^{+\cdot}$ by loss of CO_2; ions are $[CH_2Cl_2]^{2+}$ etc.

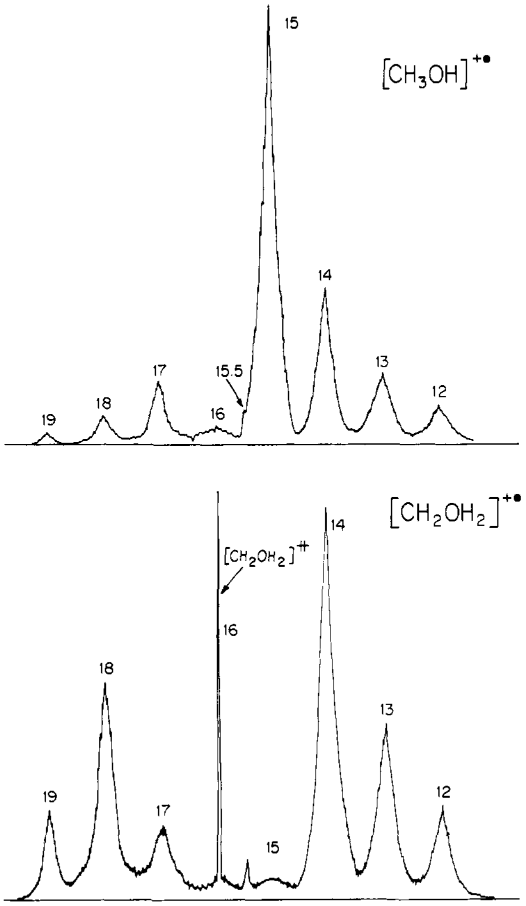


Figure 1. Partial collisional activation mass spectra of $[CH_4O]^{+\cdot}$ isomers, each corrected for contributions from $^{13}CH_3O^+$.

The enthalpy of formation, ΔH_f, of the ion–dipole complex **3** was obtained from the appearance energy (AE) of m/z 32 from $HOCH_2CH_2OH$ and $HOCH_2CHO$; they were measured with energy selected electrons.[8] The AE values were 11.42 ± 0.05 and 10.42 ± 0.05 eV, respectively, and neither required correction for contribution from $[^{13}CH_3O]^+$. The derived ΔH_f values were 197 and 193 kcal mol^{-1}. ($\Delta H_f[HOCH_2CH_2OH] = -92.6$ kcal mol^{-1},[9] $\Delta H_f[CH_2O] = -26.0$ kcal mol^{-1},[9] $\Delta H_f[CO] = -26.4$ kcal mol^{-1}, $\Delta H_f[HOCH_2CHO] = -74$ kcal mol^{-1}.[10,11]) Thus **3** is 7 ± 2 kcal mol^{-1} thermodynamically more stable than its isomer $[CH_3OH]^{+\cdot}$, $\Delta H_f = 202$ kcal mol^{-1},[12] in fair agreement with the ab initio calculations,[5] which gave **3** to be more stable by 11 kcal mol^{-1}. This complex ion may be represented as ionized methylene ($\Delta H_f = 333$ kcal mol^{-1} [12]) bonded to the dipolar water molecule ($\Delta H_f = -57.8$ kcal mol^{-1} [12]), a combination of lower energy than the (separated) inverse pair ($\Delta H_f[H_2O]^{+\cdot} = 233$ kcal/mol^{-1},[12] $\Delta H_f[CH_2] = +93.7$ kcal mol^{-1} [12]).

That **3** does not isomerize to $[CH_3OH]^{+\cdot}$ is indicated by the different shapes of the metastable peaks for the common fragmentation reaction of lowest energy requirement, namely loss of H·. That for $[CH_3OH]^{+\cdot}$ is of medium intensity and is Gaussian type; the kinetic-energy release, calculated from the peak width at half-height, $T_{0.5}$, is 0.009 ± 0.002 eV. The corresponding peak for **3**, is more intense, also of Gaussian shape, but broader; $T_{0.5} = 0.034 \pm 0.002$ meV. $[CH_2OH_2]^{+\cdot}$ displays no other metastable peaks in its mass spectrum. Because these peaks have such different characteristics, we conclude that **3** and $[CH_3OH]^{+\cdot}$ do not interconvert at internal energies up to the calculated threshold for this fragmentation, ca. 26 kcal above the enthalpy of **3**. ($\Delta H_f[CH_2OH]^+ = 169$ kcal mol^{-1},[10] $\Delta H_f[H\cdot] = 52$ kcal mol^{-1}.[12]) $\Delta H_f[CH_2CH_2OH_2]^{+\cdot}$, **1**, produced by loss of CH_2O from ionized propane-1,3-diol, gave AE(m/z 46) = 10.98 ± 0.1 eV; a small correction was required for a natural isotopic abundance contribution from $[^{13}CCH_5O]^+$. The above together with $\Delta H_f[HOCH_2CH_2CH_2OH] = -97.7$ kcal mol^{-1} [11] yields $\Delta H_f(\mathbf{1}) = 181 \pm 2$ kcal mol^{-1}. Thus, this ion–dipole complex is 5 ± 2 kcal mol^{-1} thermodynamically more stable than its isomers: $\Delta H_f[CH_3CH_2OH]^{+\cdot} = 185$ kcal mol^{-1};[12] $\Delta H_f[CH_3OCH_3]^{+\cdot} = 186$ kcal mol^{-1}.[12] The fourth $[C_2H_6O]^{+\cdot}$ isomer, $[CH_2HOCH_3]^{+\cdot}$, was generated by the loss of CH_2O from ionized 2-methoxyethanol, AE(m/z 46) = 10.45 ± 0.05 eV and $\Delta H_f[HOCH_2CH_2OCH_3] = -88.1$ kcal mol^{-1},[11] whence $\Delta H_f[CH_2HOCH_3]^{+\cdot} = 176 \pm 1$ kcal mol^{-1}; this isomer has the lowest ΔH_f.

We have identified a series of related complex ions, as indicated by the results in Table I. Analogous dissociative ionizations were used to generate these ions; all had CA and charge-stripping mass spectra significantly different from those of their counterparts of conventional structure. The table shows only doubly charged ions and fragments produced by collisional ionization because these best characterize the ion–dipole complexes. Complete results and related observations will be reported elsewhere. It should be evident that these and similar species must be present in mass spectra where they have hitherto lain unsuspected. They provide a stimulus for further investigations; for example, it is important to establish the parameters that control their stability relative to conventional ionic counterparts. It is also possible that such small stable ions are present in interstellar clouds.

Registry No. $CH_3OH^{+\cdot}$, 12538-91-9; $CH_3NH_2^{+\cdot}$, 34516-31-9; $CH_3SH^{+\cdot}$, 53369-41-8; $CH_3Cl^{+\cdot}$, 12538-71-5; $CH_3Br^{+\cdot}$, 12538-70-4; $CHClClH^{+\cdot}$, 58165-12-1; $CH_2OH_2^{+\cdot}$, 25765-84-8; $CH_2NH_3^{+\cdot}$, 21444-88-2; $CH_2SH_2^{+\cdot}$, 81255-83-6; $CH_2ClH^{+\cdot}$, 81255-84-7; $CH_2BrH^{+\cdot}$, 81255-85-8; $CH_2CH_2OH_2^{+\cdot}$, 60786-90-5; $CH_2HOCH_3^{+\cdot}$, 79802-70-3.

---

(8) The apparatus used for these measurements is described in Lossing (Lossing, F. P.; Traeger, J. C. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 9).

(9) Pedley, J. B.; Rylance, J. Sussex-NPL Computer Analyzed Thermochemical Data; Organic and Organometallic Compounds. University of Sussex, Sussex, England, 1977.

(10) By additivity,[11] using C-$(H)_2(O)(CO) = -7.0$ kcal mol^{-1}.

(11) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(12) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl. 1*, **1977**, 6.

(13) Holmes, J. L.; Terlouw, J. K.; Burgers, P. C.; Rye, R. T. B. *Org. Mass Spectrom.* **1980**, *15*, 149.