The Isomeric [C₂H₆O₂]·⁺ Hydrogen-Bridged Radical Cations [CH₂–O(H)···H···O=CH₂]·⁺, [CH₃–O···H···O=CH₂]·⁺, and [CH₃–O(H)···H···O=CH]·⁺: Theory and Experiment

Peter C. Burgers,[†] John L. Holmes,*[‡] Cornelis E. C. A. Hop,[‡,§] Ron Postma,[⊥] Paul J. A. Ruttink,[⊥] and Johan K. Terlouw*[§]

Contribution from the Analytical Chemistry Laboratory, Utrecht University, 3522 AD Utrecht, The Netherlands, Département de Chimie, Université Laval, G1K 7P4, Québec, Canada, Theoretical Chemistry Group, Utrecht University, 3508 TB Utrecht, The Netherlands, and Chemistry Department, University of Ottawa, Ontario K1N 6N5, Canada. Received January 20, 1987

Abstract: From a combination of mass spectrometry based experiments and high-level molecular orbital theory calculations, three new, thermodynamically stable isomers of ionized ethylene glycol, [CH₂OHCH₂OH]·⁺ (**1**), have been identified. These are the hydrogen-bridged radical cations [CH₂—O(H)···H···O=CH₂]·⁺ (**2**), [CH₃—O···H···O=CH₂]·⁺ (**3**), and [CH₃—O-(H)···H···O=CH]·⁺ (**4**); a fifth isomer, also H-bridged, [CH₂=CHO···H···OH₂]·⁺, has been previously reported. The ion [CH₃—O···H···O=CH₂]·⁺ (**3**) was experimentally identified (via a double collision experiment) as the stable ion formed by loss of CO from ionized methyl glycolate, whereas **2** was proposed to be a long-lived, rearranged form of ionized glycol, **1**. The common unimolecular dissociations of **2** and **3** into CH₃OH₂⁺ and HCO· were associated with energy barriers attributed to their rearrangement into (energy-rich) ions of structure **4**, from which the dissociation proceeds by direct bond cleavage. This study underlines the important role that –O···H···O– hydrogen-bridged radical cations can play in the gas-phase ion chemistry of oxygen-containing compounds and is another example of the successful combination of theory and experiment in gas-phase ion chemistry.

The low-energy dissociations of radical cations in the gas phase often only occur from isomeric ions generated via extensive rearrangement processes. This is especially true for, but by no means limited to, those ions which have half-lives of ≥10⁻⁵ s, i.e., the metastable ions which decompose in the drift regions of a mass spectrometer. The quasi-equilibrium theory provides a rationale, in that it stipulates that dissociation of metastable ions is strongly dependent on the overall activation energy rather than only the mechanistic complexity of the reaction.[1] Among the many well-documented cases, ionized methyl isobutyrate, (CH₃)₂CH-COOCH₃, provides a classical example.[2] The loss of CH₃· from these ions occurs only by C–C cleavage in the isomeric radical cation [CH₃CH₂CH=C(OH)(OCH₃)]·⁺, whose formation involves inter alia a 1,2 shift of the protonated ester moiety.

In the context of rearrangement processes, *hydrogen-bridged ions* increasingly are being proposed as stable intermediates in the dissociation of a wide range of oxygen-containing ions.[3] A good example of such species is described in a recent review,[3a] where Morton rationalizes the abundant loss of HĊO from metastable 2-methoxyethanol ions by the reaction sequence in eq 1. The internally hydrogen-bonded neutral molecule[4] upon
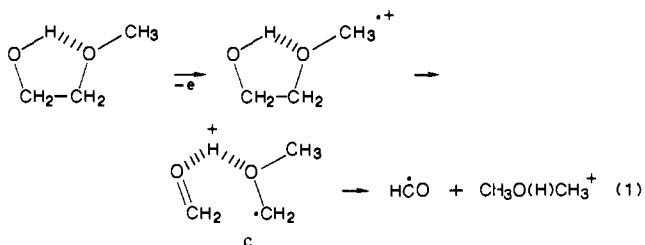
ionization rearranges via C–C bond cleavage into the hydrogen-bridged radical cation c. Since the hydrogen atom affinity of [CH₂–O(H)–CH₃]·⁺ is greater than the C–H bond strength in formaldehyde, H· transfer occurs to produce protonated dimethyl ether and a formyl radical.

Although high-level ab initio calculations do indicate that odd-electron H-bridged ions having an –O···H···O– bridge (e.g.,

[CH₂=CH—O···H···OH₂]·⁺) are quite stable species in the gas phase,[5] it should be emphasized that unambiguous experimental evidence for their existence either as stable intermediates or as product ions is not yet available. This is largely because the structural information obtained from the techniques commonly employed to characterize isomeric ion structures[6] (metastable ion (MI) and collisional activation (CA) mass spectra) cannot reliably be used to distinguish unambiguously between those isomers which may have closely similar dissociation charactersitics. In such cases, a knowledge of the barrier heights separating the isomers is essential; this information may be obtained from extensive ab initio calculations. For example, the hydrogen-bridged ion [CH₂=CH—O···H···OH₂]·⁺ is expected to have MI and CA characteristics very close to those of the isomeric distonic[7] ions [H₂O—CH₂—CHOH]·⁺ and [CH₂—CH(OH)OH₂]·⁺.[8] A different situation obtains for the *even*-electron counterparts of these ions, the well-known proton-bound dimers,[3a,9] which are readily generated in ion–molecule reactions,[9] and which have also been identified as product ions in dissociative ionization reactions.[10]

(1) (a) Levsen, K. *Fundamental Aspects of Organic Mass Spectrometry*; Verlag Chemie: New York, 1978. (b) Baer, T. In *Ionic Processes in the Gas Phase*, (NATO ASI Series); Almoster Ferreira, M. A., Ed.; Reidel Publishers: Dordrecht, 1984; Vol. 118, p 205.

(2) Göksu, E.; Weiske, T.; Halim, H.; Schwarz, H. *J. Am. Chem. Soc.* **1984**, *106*, 1167.

(3) (a) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. (b) Heinrich, N.; Schmidt, J.; Schwarz, H.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1317 and references cited therein.

(4) Caminati, W.; Wilson, E. B. *J. Mol. Spectrosc.* **1980**, *81*, 356.

(5) (a) Postma, R.; Ruttink, P. J. A.; van Duijneveldt, F. B.; Terlouw, J. K.; Holmes, J. L. *Can. J. Chem.* **1985**, *63*, 2798. (b) Postma, R.; van Helden, S.; Ruttink, P. J. A.; van Lenthe, J. H.; Terlouw, J. L.; Holmes, J. L. *Org. Mass Spectrom.*, in press.

(6) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

(7) For a definition see: Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805.

(8) Telouw, J. K.; Heerma, W.; Burgers, P. C.; Holmes, J. L. *Can. J. Chem.* **1984**, *62*, 289.

(9) See, for example: (a) Kebarle, P.; Searles, S. K.; Zolla, A.; Scarborough, J.; Arshadi, M. *J. Am. Chem. Soc.* **1967**, *89*, 6393. (b) Morton, T. H.; Beauchamp, J. L. *Ibid.* **1972**, *94*, 3671. (c) Bowers, M. T., Ed.; *Gas Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. II. (d) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 6255. (e) Larson, J. W.; Clair, R. L.; McMahon, T. B. *Can. J. Chem.* **1982**, *60*, 542. (f) Raghavachari, K.; Chandrasekhar, J.; Burnier, R. C. *J. Am. Chem. Soc.* **1984**, *106*, 3124.

(10) van Driel, J. H.; Heerman, W.; Terlouw, J. K.; Halim, H.; Schwarz, H. *Org. Mass Spectrom.* **1985**, *20*, 665.

†Université Laval.
‡University of Ottawa.
§Analytical Chemistry Laboratory, Utrecht University.
⊥Theoretical Chemistry Group, Utrecht University.

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Apart from –O···H···O– bridged odd and even electron ions, –C···H···O– bridged species have also recently been proposed both among *even*-electron ion systems[11] (*sec*-C_3H_7/H_2O^+, *t*-C_4H_9/H_2O^+, and C_3H_7/CH_3OH^+) and *odd*-electron ions[12] ($C_2H_4/H_2O^{•+}$, $C_3H_6/H_2O^{•+}$, and $C_2H_2O/H_2O^{•+}$). The *odd*-electron systems have been investigated by high-level ab initio calculations which show that the barriers for their interconversion with distonic ions (e.g., $[CH_2—CH_2—OH_2]^{•+} \leftrightarrow [CH_2—C(H)···H···OH_2]^{•+}$) are very low,[12] thus rendering impossible their separate identification with the presently available experimental techniques. A similar situation may well obtain for the corresponding *even*-electron –C···H···O– bridged species, for which computational studies have not yet been published.

With the aim of unambiguously identifying –O···H···O– bridged radical cations as stable species in the gas phase, we have investigated the structure of the $[C_2H_6O_2]^{•+}$ product ions generated by the dissociative ionization of methyl glycolate:

$$HOCH_2COOCH_3 \rightarrow [C_2H_6O_2]^{•+} + CO + e^-$$
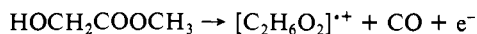
The dissociation characteristics of these $[C_2H_6O_2]^{•+}$ ions, in particular the metastable loss of H$\dot{C}$O, are prima facie close to those of ionized ethylene glycol, $[CH_2OHCH_2OH]^{•+}$ (**1**), or its –O···H···O– bridged isomer, $[CH_2O(H)···H···O=CH_2]^{•+}$ (**2**).
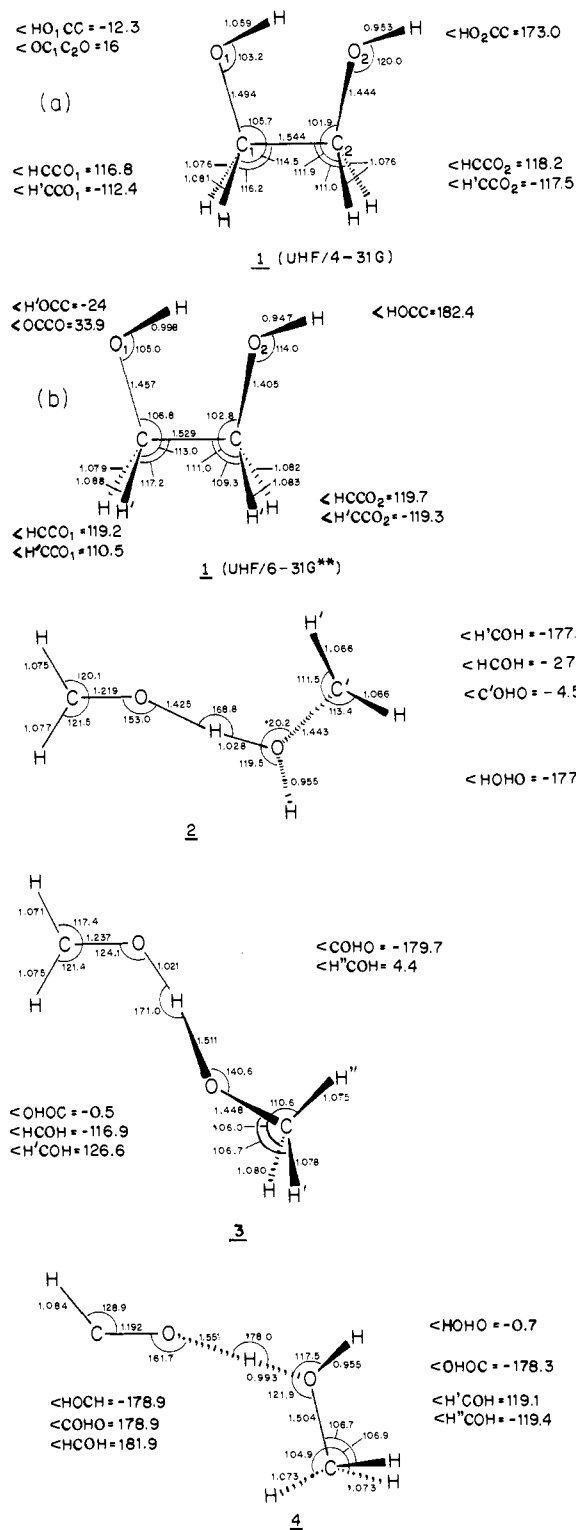
To prove that the methyl glycolate $[C_2H_6O_2]^{•+}$ ions are neither **1** nor **2** but hydrogen-bridged ions of structure $[CH_3O···H···O=CH_2]^{•+}$, (**3**) and that the common loss of H$\dot{C}$O from **1**, **2**, and **3** involves rearrangement via a high barrier into $[CH_3O(H)···H···O=CH]^•$ (**4**), we will first examine the relative stability of ions **1** to **4** by ab initio calculations and then use the results to interpret experiments on the gas-phase ion chemistry of the $[C_2H_6O_2]^{•+}$ ions derived from glycol and methyl glycolate.

Integration of the computational results with the experimental findings will then be used to construct a potential energy diagram relating **1**, **2**, **3**, and **4** and their metastable dissociation characteristics.

Theoretical Methods and Results

Standard LCAO–MO–SCF calculations were performed using the program GAMESS[13] employing restricted[14,15] and unrestricted[16] Hartree–Fock procedures, RHF and UHF, respectively. The basis sets used were the standard 4-31G[17] and 6-31G**[18,19] basis sets. Four $[C_2H_6O_2]^{•+}$ isomers were considered: $[CH_2OHCH_2OH]^{•+}$ (**1**, ionized glycol) and three hydrogen-bridged ions $[CH_2—O(H)···H···O=CH_2]^{•+}$ (**2**), $[CH_3—O···H···O=CH_2]^{•+}$ (**3**), and $[CH_3—O(H)···H···O=CH]^{•+}$ (**4**), all of which were found to be local minima on the potential energy surface.

Geometries were optimized at the UHF/4-31G level of theory. For **1** this procedure caused problems of convergence, which were associated with optimizing the geometry. It was found that the force constant of one of the parameters in the glycol ion **1** (HOCC torsion, see Figure 1a) was rather small, giving rise to numerical instability. On the 6-31G** level, however, this particular force constant became larger by a factor of 10 and it was therefore no longer numerically unstable. So the glycol structure was fully optimized at this level of theory. In order to get comparable results

(11) (a) Meot-Ner (Mautner), M.; Ross, M. M.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4839. (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665. (c) Blanchette, M. C.; Holmes, J. L.; Hop, C.E.C.A.; Lossing, F.P.L.; Postma, R.; Ruttink, P.J.A.; Telouw, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 7589.

(12) (a) Postma, R.; Ruttink, P. J. A.; van Baar, B.; Terlouw, J. K.; Holmes, J. L.; Burgers, P. C. *Chem. Phys. Lett.* **1986**, *123*, 409. (b) Postma, R.; Ruttink, P. J. A.; Terlouw, J. K.; Holmes, J. L., in preparation. (c) Postma, R.; Ruttink, P. J. A.; Terlouw, J. K.; Holmes, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 683.

(13) (a) Dupuis, M. Spangler, D.; Wendolowski, J. *NRCC Software Catalog*; Program No. QG01 (GAMESS), 1980; Vol. 1. (b) Guest, M. F.; Kendrick, J. GAMESS *User Manual, An Introductory Guide*, CCP/86/1; Daresbury Laboratory, 1986.

(14) Binkly, J. S.; Pople, J. A.; Dobosh, P. A. *Mol. Phys.* **1974**, *28*, 1423.

(15) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(16) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

(17) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(18) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

(19) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

Figure 1. Optimized UHF/4-31G and UHF/6-31G** structure of ionized ethylene glycol, **1**, and the three UHF/4-31G optimized hydrogen-bridged species, **2**, **3**, and **4**. Bond lengths are given in angstroms and bond angles in degrees.

with the other isomers **2**, **3**, **4**, the 4-31G geometry optimization of the glycol ion was restarted with the 6-31G** optimized structural parameters, and indeed convergence was achieved. Only because of computational expense, the isomers **2**, **3**, and **4** which gave no convergence problems associated with the geometry optimization were optimized at the 4-31G level of theory. The results are shown in Figure 1.

According to the results denoted as UHF/6-31G**//4-31G and UHF/6-31G**//6-31G** for the glycol in **1** in Table I, the

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Table I. Calculated Total Energies (Hartrees), Zero-Point Vibrational Energies (ZPVE, kcal mol⁻¹), and Experimental Heats of Formation (kcal mol⁻¹) of $C_2H_6O_2$·⁺ Structures and Component Systems, Based on HF/4-31G (//4-31G) and HF/6-31G** (//6-31G**) Optimized Structures

species	symmetry	RHF/4-31G	UHF/4-31G[a]	UHF/6-31G**[b]	UHF/6-31G**[b]	E_{Pople}SD-CI[b]	ZPVE[c]	$\Delta H_f°$
1	C_1	-228.276 45	-228.279 19	-228.612 22	-228.616 80	-228.707 59	55.0	142[30]
2	C_1	-228.289 26	-228.292 05	-228.623 76		-228.725 09	52.2	
3	C_1	-228.286 93	-228.289 22	-228.626 25		-228.713 34	53.5	
4	C_1	-228.298 35	-228.300 99	-228.634 72		-228.739 19	53.1	
CH_2OH^+	C_s	-113.981 29		-114.161 58		-114.201 48	26.7	168[31b]
$CH_2OH·$	C_s	-114.239 20	-114.242 29	-114.413 42		-114.453 47	24.5	-6[31c]
$CH_3O·$	C_s	-114.260 82	-114.262 77	-114.422 75		-114.464 36	25.8	4[31c]
$CH_3OH_2^+$	C_s	-115.190 17		-115.355 28		-115.421 13	42.3	135[31b]
HCO·	C_s	-113.067 33	-113.070 68	-113.248 47		-113.284 50	9.0	9[31c]
$CH_2OH_2·^+$	C_s	-114.543 17	-114.545 77	-114.709 36		-114.754 41	33.3	135[31b]
CH_2O	C_{2v}	-113.692 62		-113.868 78		-113.921 62		-28[31a]

[a] S^2 values for 4-31G and 6-31G** are 0.76. [b] See text. [c] UHF/4-31G//UHF/4-31G.

energy deviation induced by using a smaller basis for the geometry optimization is only 0.0048 hartree or 3 kcal mol⁻¹. Such a small deviation was computed too for the hydrogen-bridged species [CH₂CHO···H···OH₂]⁺, from the CH₂CHOH/H₂O·⁺ system.[5] These results indicate that the 4-31G optimized structures are good approximations to the 6-31G** optimized structures from an energetical point of view.

It is seen that in ionized glycol, **1**, one of the hydroxyl hydrogen atoms lies in between the two oxygen atoms resulting in a short distance (1.474 Å, not shown in Figure 2) for bridging with the adjacent hydroxyl group. This indicates a strong binding interaction (a feature also prominent in the neutral molecule[20]) which facilitates the isomerization into the hydrogen-bridged species **2**. For the ions **2**, **3**, and **4** the optimized geometries all have slightly bent –O···H···O– bridges with a short O–O distance, ranging from 2.453 to 2.544 Å, which compares well with those found in proton-bound dimers.[5]

Relative energies of the four ions were obtained as follows. Using the 4-31G optimized geometries single point calculations were performed at the UHF/6-31G** level. Next, using the same 4-31G optimized geometries single + double excitation configuration interaction (SD-CI) calculations were performed (ATMOL package[21a,b] and DIRECT-CI program[21c]) at the 4-31G level. The CI results were size consistency corrected using the formula described by Pople:[22] $E_{Pople} = E_{SCF} + E_{corr} [(n^2 + 2n \tan^2 2\theta)^{1/2} - n]/2(\sec 2\theta - 1)$, where E_{corr} represents the correlation energy, $E_{corr} = E_{CI} - E_{SCF}$. θ is defined through $C_0 = \cos \theta$, C_0 being the coefficient of the SCF reference configuration (RHF/4-31G results in Table I) and n the number of correlated electrons ($n = 25$ in these calculations, because the inner-shell orbitals were frozen).

The best relative energies from this work, denoted as $E_{ZPVE,Pople}/6-31G**$ values, were then obtained using the formula given by Bouma et al.[23]

$$\Delta E_{Pople}/6\text{-}31G** \approx \Delta E_{Pople}/4\text{-}31G + \Delta E(UHF/6\text{-}31G**) - \Delta E(UHF/4\text{-}31G)$$

with the addition of a contribution for the zero-point vibrational energy.

Such additivity schemes are very useful when the size of the system precludes CI calculations with polarized basis sets, and are used frequently.[23,24] They have been tested extensively by

Table II. Calculated and Experimental Relative Energies (kcal mol⁻¹) of $C_2H_6O_2$·⁺ Structures and Component Systems

species	E_{rel}[a]	exptl
$HOCH_2CH_2OH·^+$ (**1**)	0	142
$H_2CO···H···O(H)CH_2·^+$ (**2**)	-13	
$H_2CO···H···OCH_3·^+$ (**3**)	-8	
$HCO···H···O(H)CH_3·^+$ (**4**)	-22	
$CH_2OH^+ + CH_2OH·$	+19	162
$CH_2OH^+ + CH_3O·$	+20	172
$CH_2OH_2·^+ + CH_2O$	+16	167
$CH_3OH_2^+ + HCO·$	-5	144

[a] SD-CI/6-31G** values (see text) including ZPVE contributions.

McKee and Lipscomb[25] who found an approximate deficiency of 2 kcal mol⁻¹ for systems involving simple geometry changes and ~4 kcal mol⁻¹ for systems involving dimerization and molecular combination. These additivity schemes have also been tested for the more difficult open-shell systems by Radom et al.,[26] and they found an error of ~3 kcal mol⁻¹. Furthermore the additivity scheme, as given in this paper, has recently been tested for the hydrogen-bridged species [CH₂CHO···H···OH₂]·⁺, the ionized vinyl alcohol/water system, and an error of 1.5 kcal mol⁻¹ was computed.[5b]

Harmonic vibrational frequencies have been calculated at the HF level with the split-valence 4-31G basis[27] at geometries optimized with this basis set. These were used to calculate the zero-point vibrational energies. The results are also in Table I. HF calculations are known[28] to overestimate vibrational frequencies by ~10% and so the zero-point vibrational energy contributions to relative energies have been obtained by scaling the calculated HF/4-31G zero-point energies by a factor of 0.9.

The relative energies of the four isomeric ions and component systems are given in Table II using ionized glycol **1** as the reference point. It is seen that all three hydrogen-bridged species are thermodynamically more stable than ionized glycol. At the present level of theory, comparison of these relative energies with those derived from the direct bond cleavage dissociation products of lowest energy requirement, i.e.

$$2 \rightarrow CH_2OH^+ + CH_2OH·$$

$$3 \rightarrow CH_2OH^+ + CH_3O·$$

$$4 \rightarrow CH_3OH_2^+ + HCO·$$
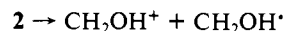
is less satisfactory. Note that satisfactory calculations of the relative energies of the CH₃O· and CH₂OH· neutrals involved in these reactions require computations at a level of theory[29] which,

(20) van Alsenoy, C.; van den Enden, L.; Schafer, L. THEOCHEM **1984**, *108*, 121.

(21) (a) Saunders, V. A. ATMOL4: molecular integrals for contacted spherical harmonic Gaussian orbitals, 1979. (b) Saunders, V. A.; Guest, M. F. ATMOL, SCF Program (1976). (c) The DIRECT-CI method: Saunders, V. A.; van Lenthe, J. H. *Mol. Phys.* **1983**, *48*, 923.

(22) Pople, J. A.; Seeger, R.; Krishan, R., *Int. J. Quantum Chem.* **1977**, *11*, 149.

(23) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 1743.

(24) (a) Krogh-Jespersen, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J., *J. Am. Chem. Soc.* **1979**, *101*, 4843. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5649. (c) Bouma, W. J.; Gill, P. M. W., Radom, L. *Org. Mass Spectrom.* **1984**, *19*, 610.

(25) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673.

(26) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497.

(27) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(28) Pople, J. A.; Schlegel, H. B.; Krishan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F., Jr.; Hehre, W. J. *Int. J. Quantum Chem.* **1981**, *15*, 269.

(29) Saebo, S.; Radom, L.; Schaefer, H. F., III. *J. Chem. Phys.* **1983**, *78*, 845.

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Table III. Collisional Activation (CA) Mass Spectra[a] of the $[C_2H_6O_2]^{\cdot+}$ Ions

precursor molecule	neutral lost	daughter Ion m/z																
		12	13	14	15	28	29	30	31	32	33	42	43	44	45	46	47	61
CH_2OHCH_2OH		<1	<1	1	3	5	31	15	200	52	1000[b]	2	7	9				15
$CH_2OHCOOCH_3$	CO	<1	<1	2	15	9	112	53	668	166	1000[b]		1	5	1	1	3	275
$CH_3CH_2COOH^c$		<1	<1	6	20	110	1000	30	5	2	7	9	100	20	750[b]		110	20
$CH_3OOCH_3^c$		2	5	20	200		550	270[b]	920[b]	80	20				6	4	45	1000

[a] Intensities normalized to the highest peak in the CA mass spectrum.   [b] Also present in the MI mass spectrum.   [c] Unpublished spectra recorded in this laboratory.

in view of the expenses involved, cannot reasonably be achieved for the $[C_2H_6O_2]^{+\cdot}$ system.

However, using the well-defined experimental heat of formation of ionized glycol, $\Delta H_f^\circ[1] = 142$ kcal mol^{-1} [30] (see next section), with the relative energies for **2**, **3**, and **4** in Table I, ΔH_f° values for **2**, **3**, and **4** of 129, 134, 120 kcal mol^{-1} are obtained. Using experimental ΔH_f° values from ref 31 for the dissociation products in the above reactions, it is found that **2**, **3**, and **4** are stable by $\sim$34, $\sim$39, and $\sim$25 kcal mol^{-1} relative to their energetically most favored direct bond cleavage reactions.

The question of the barrier involved in the isomerization of **1** into **2**, which will be considered further in the next section, was also addressed computationally. Note (see above) that the optimized structure of **1** has a strong hydrogen bridge to facilitate the isomerization into **2**, which is lower in energy. Unfortunately all attempts to locate a transition state for **1** or **2** at the UHF/4-31G level were unsuccessful, but the results indicate that the barrier cannot be substantial. In view of the experimental evidence described below and the computational expenses involved, other isomerization pathways, i.e., **2 → 4**, **2 → 3**, and **3 → 4**, were not investigated by theory.

Gas-Phase Ion Chemistry of Ethylene Glycol. Formation of $[CH_2—O(H)\cdots H\cdots O=CH_2]^{\cdot+}$ (2)

The molecular ion of ethylene glycol, $[CH_2OHCH_2OH]^{\cdot+}$ (**1**), abundantly undergoes one reaction in the microsecond time frame, to produce $[CH_3OH_2]^+$ and $H\dot{C}O$. The m/z 33 peak is the second most intense in the normal mass spectrum (30%, vs. m/z 31 = 100%). The structures of the ionic and neutral fragment were determined from their collisional activation (CA) and collisionally induced dissociative ionization (CIDI)[32] mass spectra, respectively. The kinetic energy release of this unimolecular reaction, as measured from the peak width at half-height $T_{0.5}$, is 13 meV. The appearance energy (AE) of this metastable process was obtained using a comparative method,[33] AE = 10.65 ± 0.1 eV, which is $\sim$0.4 eV in excess of the calculated value, 10.3 ± 0.1 eV (from $\Delta H_f^\circ[CH_2OHCH_2OH] = -92.6$ kcal mol^{-1},[34] $\Delta H_f^\circ[CH_3OH_2]^+$ = 135.5 kcal mol^{-1},[31b] and $\Delta H_f^\circ[H\dot{C}O]$ = 9 kcal mol^{-1};[31c] this AE corresponds to a transition state energy of 152 ± 3 kcal mol^{-1}. The ionization energy of CH_2OHCH_2OH has been assessed as 10.16 ± 0.05 eV,[30] and thus the minimum energy requirement for the metastable process is 0.49 ± 0.15 eV. This activation energy is probably too small to allow the molecular ion to be metastable (i.e., to fragment in the microsecond time frame); the necessary density of states will not be sufficiently great unless there is a thermochemically more stable isomeric ion to which the glycol molecular ion can readily rearrange. In any case, one can be confident that in order to generate $[CH_3OH_2]^+$ + $H\dot{C}O$ as fragmentation products, the initially formed molecular ion *must*

rearrange to an intermediate ion having a lower ΔH_f° than that of $[CH_2OHCH_2OH]^{\cdot+}$. In agreement with the above, the loss of H$\cdot$ from *unrearranged* **1** by α-cleavage has a calculated activation energy of only 0.5 eV and $[M - H]^+$ is not observed in the MI mass spectrum ($\Delta H_f^\circ[CH_2OHC^+HOH]$ = 102 kcal mol^{-1} [35] and $\Delta H_f^\circ[H\cdot]$ = 52 kcal mol^{-1} [31a]). An attractive intermediate ion is the hydrogen-bridged structure **2** whose formation
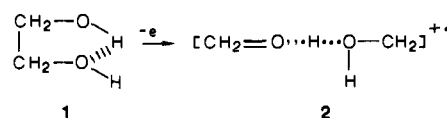
only requires C–C bond cleavage in the hydrogen-bridged precursor ion and which ab initio calculations predict to be lower in energy by 13 kcal mol^{-1} (see above). A 1,5-hydrogen transfer would then produce $[CH_3—O(H)\cdots H\cdots O=CH]^{\cdot+}$ (**4**), from which $CH_3OH_2^+$ + H$\dot{C}O$ are formed by direct bond cleavage. Note, however, that although **4** is calculated to be a very stable ion, the isomerization **2 → 4** must involve a significant energy barrier because the dissociation products $[CH_3OH_2]^+$ and H$\dot{C}O$ are not formed at the thermochemical threshold. The transition state for such a fragmentation will involve the bending of the linear O–H–O bridge, an energy-demanding process.

The collisional activation (CA) mass spectrum of ions **1** (Table III), obtained ca. 10^{-5} s after their formation, lends strong support to the proposed isomerization **1 → 2**. The observed intensity distribution rules out the involvement of the "conventional" isomers $[CH_3OOCH_3]^{\cdot+}$ and $[CH_3CH_2OOH]^{\cdot+}$ (see Table III), and $[CH_3OCH_2OH]^{\cdot+}$ and $[CH_3CH(OH)_2]^{\cdot+}$ can be rejected because the latter two ions would abundantly lose H$\cdot$ and/or $CH_3\cdot$ and/or H_2O upon collisional activation. For example, the ion $[CH_3CH(OH)_2]^{\cdot+}$ (so far not observed mass spectrometrically) is expected, on thermochemical grounds, to show peaks at m/z 47 and 44 in the CA mass spectrum because $\Delta H_f^\circ([CH(OH)_2]^+) + \Delta H_f^\circ[CH_3\cdot]$ = 133 kcal mol^{-1},[31c,36] and $\Delta H_f^\circ([CH_2CHOH]^{\cdot+} + \Delta H_f^\circ[H_2O]$ = 123 kcal mol^{-1},[31,37] whereas the observed transition-state energy for dissociation into $[CH_3OH_2]^+$ + HCO is $\sim$153 kcal mol^{-1}.

Similarly, the formation of the isomeric distonic ion $[HO-CH-CH_2-OH_2]^{\cdot+}$ can be discarded, because the collision-induced H_2O loss therefrom, leading to $[CH_2=CHOH]^{\cdot+}$, m/z 44, is absent in the CA mass spectrum (ΔH_f°(products) = 123 kcal mol^{-1}). Thus a mechanism for the metastable loss of H$\dot{C}O$ from **1** involving two consecutive **1,3** H shifts, **1 →** $[HO-CH-CH_2-OH_2]^{\cdot+}$ → $CH_3OH_2^+$ + H$\dot{C}O$, can clearly be ruled out.

It is noteworthy that the CA mass spectrum of **1** contains a significant peak at m/z 32, corresponding to $[CH_4O]^{\cdot+}$ ions. It is known that two stable isomeric $[CH_4O]^{\cdot+}$ ions exist, namely $[CH_3OH]^{\cdot+}$ and the ylide ion $[CH_2OH_2]^{\cdot+}$ (ΔH_f° = respectively 202 and 194 kcal mol^{-1})[38]. To probe the structure of the collisionally generated $[CH_4O]^{\cdot+}$ ions, these were produced in the first field-free region of the mass spectrometer by collision with helium. They were then selectively transmitted through the magnet (apparent mass = 16.5) and collisionally decomposed in

(30) Holmes, J. L.; Lossing, F. P. *Can. J. Chem.* **1982**, *60*, 2365.
(31) (a) Rosenstock, H. M.; Draxl, K. K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1. (b) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (c) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.
(32) For leading references, see: (a) Wesdemiotis, C.; Feng, R.; Williams, McLafferty, F. W. *Org. Mass Spectrom.* **1986**, *21*, 689. (b) Holmes, J. L.; Mommers, A. A.; Terlouw, J. K.; Hop, C. E. C. A., *Int. J. Mass Spectrom. Ion Processes* **1986**, *68*, 249.
(33) Burgers, P. C.; Holmes, J. L. *Org. Mass Spectrom.* **1982**, *17*, 123.
(34) Pedley, J. B.; Rylance, J. *Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex, Sussex, England, 1977.

(35) Lossing, F. P., unpublished results.
(36) Holmes, J. L.; Mommers, A. A.; de Koster, C. G.; Heerma, W.; Terlouw, J. K. *Chem. Phys. Lett.* **1985**, *115*, 437.
(37) Holmes, J. L.; Terlouw, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860.
(38) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C., *J. Am. Chem. Soc.* **1982**, *104*, 2931.

Isomeric Hydrogen-Bridged [C₂H₆O₂]·⁺

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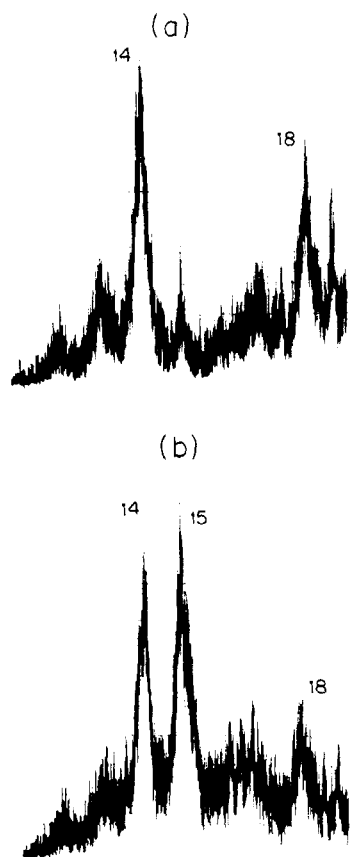
Figure 2. (a) Collisional activation (CA) mass spectrum of $[CH_4O]^{\cdot+}$ ions collisionally generated from ionized ethylene glycol. (b) CA mass spectrum of $[CH_4O]^{\cdot+}$ ions collisionally generated from $[M - CO]^{\cdot+}$, m/z 62, ions from methyl glycolate.

the second field-free region.[39] The resulting product ions were energy (mass) analyzed using the electrostatic sector. The $[CH_4O]^{\cdot+}$ ions were found to be not $[CH_3OH]^{\cdot+}$ but $[CH_2OH_2]^{\cdot+}$, a unit present in the hydrogen-bridged ion $[CH_2-O(H)\cdots H\cdots O=CH_2]^{\cdot+}$; see Figure 2a. It should be noted that the absence of the doubly charged ion $[CH_4O]^{2+}$ at m/z 16 is due to the low transitional energy of the $[CH_4O]^{\cdot+}$ ions. Ion source generated $[CH_2OH_2]^{\cdot+}$ ions with 4 kV translational energy show the same CA mass spectrum as shown in Figure 2a. All of the above results strongly indicate that $[CH_2OHCH_2OH]^{\cdot+}$ ions after their formation by electron impact have rearranged irreversibly into the hydrogen-bridged species $[CH_2-O(H)\cdots H\cdots O=CH_2]^{\cdot+}$ (2) and that this ion exists in a deep well.

Gas-Phase Chemistry of the [C₂H₆O₂]·⁺ Daughter Ion of Methyl Glycolate. Formation of [CH₃—O⋯H⋯O=CH₂]·⁺ (3)

Only one abundant unimolecular dissociation is observed in the MI mass spectrum of the m/z 62 $[C_2H_6O_2]^{\cdot+}$ ions generated by dissociative ionization of methyl glycolate, $HOCH_2COOCH_3$, namely,

$$[C_2H_6O_2]^{\cdot+} \rightarrow [CH_3OH_2]^+ + HCO^{\cdot}$$

which also characterizes the MI spectrum of ionized glycol **1**. The transition-state energy, 157 ± 3 kcal mol⁻¹ (derived from AE $(62^+ \rightarrow 33^+) = 11.48 \pm 0.1$ eV, $\Delta H_f°[ester] = 134 \pm 1$ kcal mol⁻¹,[40] and $\Delta H_f°[CO] = -26.4$ kcal mol⁻¹ [31a]) is close to that found for the ionized ethylene glycol system **1/2**. but the associated kinetic energy releases are not the same ($T_{0.5} = 27$ vs. 13 meV for **1/2**). The heat of formation of the methyl glycolate $[C_2H_6O_2]^{+\cdot}$ ions,

$\Delta H_f° < 144$ kcal mol⁻¹, was derived from the AE of the reaction $[HOCH_2COOCH_3]^{+\cdot} \rightarrow [C_2H_6O_2]^{\cdot+} + CO$, AE $= 10.9 \pm 0.2$ eV (energy-selected electrons[41]). This $\Delta H_f°$ cannot be distinguished from that of **1**, but it should be noted that it represents an *upper* limit: severe tailing was observed in the AE m/z 62 measurement and the magnitude of the kinetic energy released in the formation of the $[C_2H_6O_2]^{\cdot+}$ ions, $T_{0.5} = 140$ meV, shows that a significant kinetic shift may be present. The CA mass spectrum of the methyl glycolate $[C_2H_6O_2]^{\cdot+}$ ions is given in Table III. Apart from the weak m/z 12–15 group, the spectrum is significantly, but not greatly, different from that of (rearranged) ethylene glycol ions, **1/2**, and so the "conventional" or distonic structures discussed in the previous section again need not be considered.

The experimental results presented so far could be interpreted as showing that methyl glycolate (largely) produces $[C_2H_6O_2]^{\cdot+}$ ions of structure **1/2**. A double-collision experiment (as described in the previous section) on the corresponding m/z 32, $[CH_4O]^{\cdot+}$ ions, clearly demonstrated that this was not the case. A comparison of spectra a and b in Figure 2 shows that the $[C_2H_6O_2]^{\cdot+}$ ions from the ester obviously yield $[CH_3OH]^{\cdot+}$ in addition to the ylide ion.[42]

We propose that the ester $[C_2H_6O_2]^{\cdot+}$ ions are hydrogen-bridged ions of structure $[CH_3-O\cdots H\cdots O=CH_2]^{\cdot+}$ (3), which upon collisional activation produce $[CH_3OH]^{\cdot+}$ by direct bond cleavage. As was shown in the theoretical section, ions **3** are found to be stable species with a calculated $\Delta H_f°$ of 134 kcal mol⁻¹, some 10 kcal mol⁻¹ below the *upper* limit derived from the AE measurements. A 1,4 hydrogen transfer involving a sizable barrier (see next section) would produce $[CH_3-O(H)\cdots H\cdots O=CH]^{\cdot+}$ (4), from which $[CH_3OH_2]^+$ and $H\overset{\cdot}{C}O$, the dissociation products of the metastable ions, **3**, are formed by direct bond cleavage.

The generation of **3** by loss of CO from the ester molecular ions could be envisaged as a carbonyl extrusion with a concomitant 1,4 hydrogen shift:
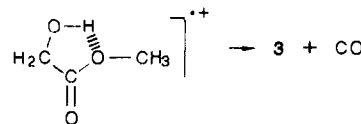
The mass spectra of the labeled esters $HOCH_2CO^{18}O^{13}CH_3$ and $HOCH_2C^{18}OOCH_3$ showed that the carbonyl $C=O$ group is indeed exclusively lost as carbon monoxide. However, by analogy with the concept proposed by Morton (see Introduction) to rationalize the gas-phase ion chemistry of $HOCH_2CH_2OCH_3$, loss of CO to produce **3** can also be envisaged as occurring from a hydrogen-bridged isomer of the ionized ester, which is also H-bonded in its neutral form, viz. eq 2. Such an isomerization can
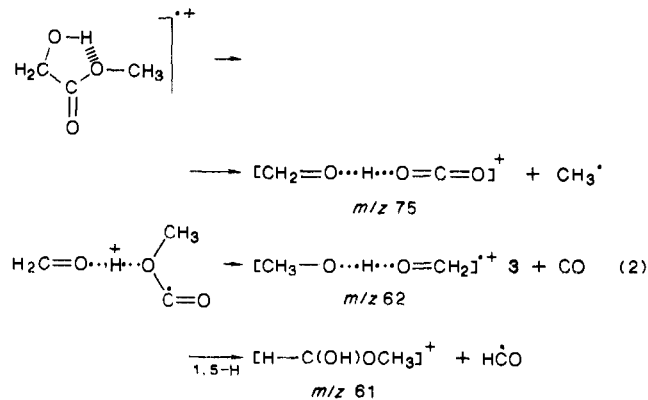
also readily explain the two other reactions in the MI mass spectrum of the ester, namely loss of $H\overset{\cdot}{C}O$ yielding m/z 61

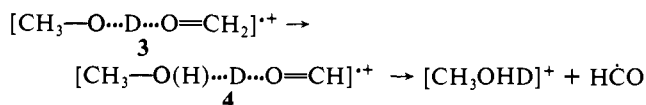(39) Villeneuve, S.; Burgers, P. C. *Org. Mass Spectrom.* **1986**, *21*, 733.

(40) Benson, S. W. *Thermodynamical Kinetics*, 2nd ed.; Wiley: New York, 1976. We assign the increments $C(H)_2(CO)_2$ and $C(H)_2(CO)(O)$ to be equal by analogy with $C(H)_3CO$ and $C(H)_3(O)$.

(41) (a) Maeda, K.; Semeluk, G. P.; Lossing, F. P. *Int. J. Mass Spectrom Ion Phys.* **1968**, *1*, 395. (b) Lossing, F. P.; Traeger, J. C. *Ibid.* **1976**, *19*, 9.
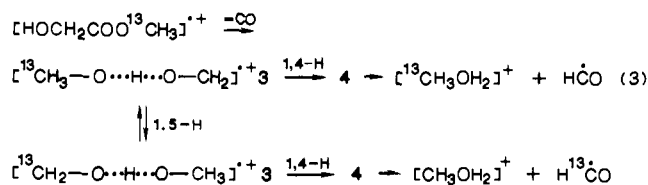
(42) A ratio of $[CH_3OH]^{+\cdot}:[CH_2OH_2]^{+\cdot} = 2:3$ for the species shown in Figure 2b was obtained from the 4-kV CA mass spectra and relative collision yields for the two $[CH_4O]^{+\cdot}$ isomers[43].

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$[C_2H_5O_2]^{\cdot+}$ ions, which were identified from their CA mass spectrum as protonated methyl formate,[43] and loss of $CH_3^\cdot$ which probably yields the CH_2O/CO_2 proton-bound dimer (the MI and CA mass spectra of which are dominated by a narrow peak at m/z 31, $[CH_2OH]^+$). The metastable loss of $CH_3^\cdot$ is associated with a large kinetic energy release, $T_{0.5}$ = 360 meV, and this can also be accounted for. The calculated AE for this loss, assuming threshold generation of the reaction products (using an estimated $\Delta H_f^\circ [CH_2\!=\!O\cdots H\cdots O\!=\!C\!=\!O]^+ \sim$ 66 kcal mol^{-1},[44] $\Delta H_f^\circ [CH_3^\cdot]$ = 35 kcal mol^{-1} [31c]), is $\sim$0.3 eV below the IE of the ester precursor molecule (10.42 eV), which is very close to the measured AE m/z 75 (10.50 eV). Thus the methyl loss indeed involves a significant barrier for its reverse reaction, in keeping with the observed large energy release.

In accord with the above mechanistic proposal, metastable m/z 63 daughter ions generated from the O–D labeled ester DOC-H$_2$COOCH$_3$, i.e., ions $[CH_3\!-\!O\cdots D\cdots O\!=\!CH_2]^{\cdot+}$, appear to lose HĊO exclusively:

$$[CH_3\!-\!O\cdots D\cdots O\!=\!CH_2]^{\cdot+} \rightarrow$$
$$\textbf{3}$$
$$[CH_3\!-\!O(H)\cdots D\cdots O\!=\!CH]^{\cdot+} \rightarrow [CH_3OHD]^+ + HĊO$$
$$\textbf{4}$$

An (almost) exclusive loss of HĊO vs. DĊO (ratio 100:6) is also observed in the MI spectrum of the m/z 65 $[CD_3\!-\!O\cdots H\cdots O\!=\!CH_2]^{\cdot+}$ ions generated from the CD$_3$-labeled ester HOCH$_2$CO-OCD$_3$. However, metastable m/z 63 $[^{13}CH_3\!-\!O\cdots H\cdots O\!=\!CH_2]^{\cdot+}$ ions generated from the ^{13}C-labeled ester HOCH$_2$COO^{13}CH$_3$ lose both HĊO and H^{13}ĊO in the ratio 100:86; in the CA spectrum, where ions of lower internal energy are sampled, the ratio is 100:52. This indicates that the preferred HĊO loss from $[CD_3\!-\!O\cdots$ H$\cdots O\!=\!CH_2]^{\cdot+}$ results from an isotope effect. These labeling experiments also show that before metastable ions **3** dissociate (via rearrangement into the reacting configuration $[CH_3\!-\!O\text{-}(H)\cdots H\cdots O\!=\!CH]^{\cdot+}$ (**4**)), their carbon atoms, via 1,5-H exchange reactions, become largely equivalent, viz. eq 3. Ab initio cal-

$$[HOCH_2COO^{13}CH_3]^{\cdot+} \xrightarrow{-CO}$$

$$[^{13}CH_3\!-\!O\cdots H\cdots O\!-\!CH_2]^{\cdot+}\textbf{3} \xrightarrow{1,4\text{-}H} \textbf{4} \rightarrow [^{13}CH_3OH_2]^+ + HĊO \quad (3)$$

$$\Big\updownarrow 1,5\text{-}H$$

$$[^{13}CH_2\!-\!O\cdots H\cdots O\!-\!CH_3]^{\cdot+}\textbf{3} \xrightarrow{1,4\text{-}H} \textbf{4} \rightarrow [CH_3OH_2]^+ + H^{13}ĊO$$

culations on $-O\cdots H\cdots O-$ bridged ions (potential scans)[5,26] indicate that the hydrogen bridge is remarkably rigid toward bending. This could explain why the equilibration of the carbon atoms (via a 1,5-H shift) is less energy demanding than the rearrangement (**3** $\rightarrow$ **4** $\rightarrow$ products) which, we propose, involves a 1,4-H transfer rather than consecutive 1,2-H ($CH_3\!-\!O\cdots H\cdots \rightarrow CH_2\!-\!O(H)\cdots\cdots H\cdots$) and 1,5-H shifts. In line with this latter proposal we observe that the cluster m/z 15–18 (relative abundances 1:10:7:100, respectively) in the CA mass spectrum of m/z 65 ions $[CD_3\!-\!O\cdots H\cdots O\!=\!CH_2]^{\cdot+}$ is dominated by m/z 18 $[CD_3]^+$. Thus the loss of HĊO from metastable m/z 65 ions produces $CD_3OH_2^+(\rightarrow CD_3^+ + H_2O)$ and not $CD_2HOHD^+(\rightarrow CD_2H^+ + HDO)$.

Conclusions

The potential energy diagram presented in Figure 3 summarizes the evidence discussed in the preceding theoretical and experimental sections on the stability and the metastable dissociation characteristics of ionized glycol **1**, and its $-O\cdots H\cdots O-$ bridged isomers **2**, **3**, and **4**.

The molecular ion of ethylene glycol, **1**, readily isomerizes into the H-bridged radical cation **2**. The latter is computed to be 13 kcal mol^{-1} more stable than **1**. The height of the barrier **1** $\rightarrow$ **2**
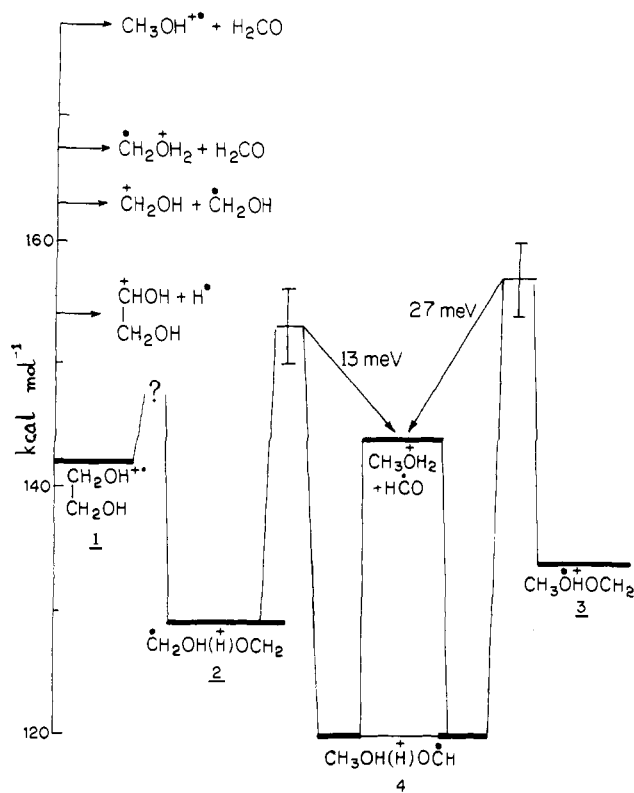
(43) van Baar, B.; Halim, H.; Terlouw, J. K.; Schwarz, H. *J. Chem. Soc., Chem. Commun.* **1986**, 728.

(44) From the relationship in ref 9d to determine ΔH_f° of proton bound dimers and using proton affinities for CO_2 and CH_2O of 131 and 171 kcal mol^{-1}, respectively.

Figure 3. Energy diagram for $[C_2H_6O_2]^{\cdot+}$ isomers.

is not known, but it must be small. It is proposed that the metastable HĊO loss from **1** proceeds via the isomerizations **1** $\rightarrow$ **2** $\rightarrow$ **4**. From excited ion **4**, which theory predicts to be remarkably stable, protonated methanol and HĊO are produced by a direct bond cleavage. The energy barrier for **1** $\rightarrow CH_3OH_2^+$ + HĊO is ascribed to the 1,5-H shift for **2** $\rightarrow$ **4**.

The $-O\cdots H\cdots O-$ hydrogen-bridged ion $[CH_3\!-\!O\cdots H\cdots OCH_2]^{\cdot+}$ (**3**) is produced by CO loss from ionized methyl glycolate. Theory predicts that **3** is also more stable than ionized glycol **1**, and careful analysis of all the evidence presented showed that it does not communicate with ions **1** and **2**. We propose that **4** is also the reacting configuration for metastable ion **3**, the reaction requiring a 1,4-H shift. The barrier to this rearrangement is higher than for **2** $\rightarrow$ **4** and this may reflect the rigidity to bending in the $-O\cdots H\cdots O-$ bridged ions. Note that the barrier heights and the associated kinetic energy releases are different; this rules out the possibility that **2** and **3** freely interconvert prior to their common metastable fragmentation.

It is remarkable that such a small fraction of the excess energy appears as translational energy of the products; $T_{0.5}$ values of this magnitude are typically associated with reactions which proceed much closer to their thermochemical threshold.[45] This behavior may be characteristic of $-O\cdots H\cdots O-$ bridged radical cations.

Experimental Section

(45) Holmes, J. L.; Terlouw, J. K. *Org. Mass Spectrom.* **1980**, *15*, 383.

mitted daughter ions. The resulting CA mass spectra were satisfactorily free from artifacts. IE and daughter ion AE values were obtained with an apparatus comprising an electrostatic electron monochromator with a quadrupole mass analyzer and minicomputer data system.[41] All other AE values were obtained by a comparative method[33] using a Kratos MS 902 mass spectrometer.

In the above experiments all slits were fully open to obtain maximum signal strength and to minimize energy resolving effects. Metastable peak shapes, however, were obtained using a main beam width of 0.2 V at an electric sector potential of 422 V, corresponding to an accelerating voltage of 8 kV. Kinetic energy releases were evaluated by established methods.[46]

Methyl glycolate was obtained by esterification of glycolic acid, CH2OHCOOH, using methanol in the usual manner. All other compounds were commercially available and their purity was checked by gas chromatography. A methanol sample containing $^{13}CH_3OH$ (80%),

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(46) Terlouw, J. K.; Burgers, P. C.; Hommes, H. *Org. Mass Spectrom.* **1979**, *14*, 387.

CH3OCH·+, a New Stable C2H4O·+ Isomer, and a Reassessment of the Oxirane·+ Potential Surface

J. M. Buschek,[†] **J. L. Holmes,**[*†] **and J. K. Terlouw**[*‡]

Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, K1N 9B4, Canada, and the Analytical Chemistry Department, Utrecht University, 3522 AD, Utrecht, The Netherlands. Received March 19, 1987

Abstract: The [C2H4O]·+ isomer of structure [CH3OCH]·+ has been shown to be unambiguously generated by CO2 loss from ionized methyl glyoxylate. $\Delta H_f°$ for this new ion was measured to be 224 ± 1 kcal mol⁻¹. The [C2H4O]·+ ion produced by the loss of CH2O from ionized 1,3-dioxolane and by the loss of HCOOH from ionized methoxymethyl formate was proposed to have the structure [CH2OCH2]·+, $\Delta H_f° = 206 ± 2$ kcal mol⁻¹. Ionized oxirane in either its ²B₁ or ²A₁ state was proposed to be generated by loss of CO2 from ionized ethylene carbonate at a threshold energy corresponding to a $\Delta H_f° = 235 ± 1$ kcal mol⁻¹. The structure assignments were aided by observations of collisional activation and metastable ion mass spectra. The common fragmentations of [CH2OCH2]·+ and [oxirane]·+ ions, loss of CH3· and H·, take place at similar high internal energies, leading to large kinetic energy releases in the metastable ion decompositions. Interpretations of the observations were in keeping with recent high-level ab initio molecular orbital theory calculations, but detailed mechanisms could not be established.

In recent years, advances in ab initio molecular orbital theory calculations and developments in experimental techniques for assigning structures to gas-phase ions have resulted in the successful, close collaboration of these methods. The role of experiment has been reviewed,[1] and theory[2] is well represented by the many contributions of Radom and his co-workers.

In an early ab initio paper,[3] the [C2H4O]·+ system was described, and it was calculated that no fewer than 11 isomers exist in potential wells; these are shown in Scheme I. At that time (1975), only **1**, **2**, and **4** had been studied by experiment, but the calculations showed that isomers **3** and **5–9** lay in sizable potential wells and so were reasonable prospects for experimental identification.

The present situation can be summarized as follows. The keto–enol pair **1** and **2** have been thoroughly investigated; their enthalpy of formation,[4a] $\Delta H_f°$, and dissociation characteristics (metastable ion (MI) fragmentations[4b] and collision-induced decompositions[4c]) are well established. The ionized hydroxy-carbene **3** not only plays an important role in the major dissociation of the enol **2**, but has also been independently generated and characterized. For this isomer too, theory[3,5a] and experiment[5b] are in excellent agreement.

Scheme I
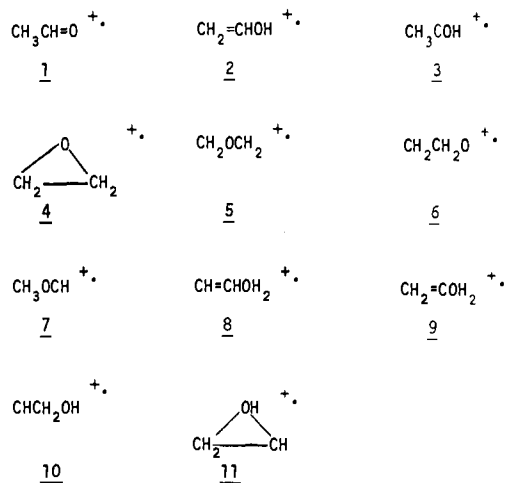
For ionized oxirane **4**, $\Delta H_f°$ (231 kcal mol⁻¹ [6]) and its MI[4b] and collisional activation (CA) mass spectra[4c] have been reported. Its

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[†] University of Ottawa.
[‡] University of Utrecht.

(1) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.