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Theory and Experiment in Concert; The $CH_3O\text{-}C^+{=}O$ Ion and Its Isomers

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Abstract: By using a combination of mass spectrometric techniques and high level ab initio molecular orbital theory calculations (Complete Active Space Self Consistent Field Procedure), eleven isomeric $[C_2H_3O_2]^+$ ion structures have been investigated. Five were believed to be clearly identified by experiment, namely $[CH_3OC^+O]$, $[HOCH_2C^+O]$, $[C^+H_2OCHO]$, $[HOC^+HCHO]$, and $[\overline{CH_2OC}{}^+OH]$; their heats of formation, $\Delta H_f°$, were 120, 124, 130, 131, and 141 kcal mol^{-1}, respectively. In this work the unusually difficult interpretation of experimental results rested heavily upon the theoretical calculations. Several hydrogen-bridged cations were considered in the calculations and two, $[H_2C{\cdots}H^+{\cdots}O{=}CO]$ and $[H_2C{=}O{\cdots}H^+{\cdots}O{=}C]$, were found to represent local minima on the $[C_2H_3O_2]^+$ potential surface. Some experimental evidence is presented for the former, which appears to be a stable isomer ($\Delta H_f° = 147$ kcal mol^{-1}) produced via the collisional excitation of $[CH_3OC^+O]$.

Structural isomerism in gas-phase ions has received steadily increasing attention during the past 10 years. By using the combined information from mass spectrometric techniques[1] and ab initio molecular orbital theory calculations,[2] the gas-phase chemistry of a number of stable ions of both familiar, e.g., $[CH_3{-}C^+{=}O]$,[3,4] and unexpected structure has been unravelled. The latter include ylide, distonic,[5] and hydrogen-bridged radical cations such as $[CH_2OH_2]^{\bullet+}$,[6a,b] $[CH_2CH_2OH_2]^{\bullet+}$,[7,8] and $[CH_2{=}CH{-}O{\cdots}H{\cdots}OH_2]^{\bullet+}$,[9] respectively. Although the ions $[CH_3{-}C^+{=}O]$ and $[HO{-}C^+{=}O]$ and their isomers have been studied in considerable detail,[3,4,10-12] the closely related $[CH_3O{-}C^+{=}O]$ ion and its $[C_2H_3O_2]^+$ isomers have received little attention.

The methoxycarbonyl cation, $[CH_3O{-}C^+{=}O]$, is frequently observed in the mass spectra of oxygen-containing compounds, and its collisional activation (CA) mass spectrum has been reported.[13] On the basis of its generation from simple methyl carboxylates, appropriate appearance energy (AE) measurements would be expected to yield a consistent heat of formation, $\Delta H_f°$, for this ion. Surprisingly, however, such a series of measurements by Briggs and Shannon[14] yielded $\Delta H_f°$ values varying from 133 to 153 kcal/mol. Dissociative ionization of ICH_2COOH has been proposed to yield a second isomer, $[C^+H_2{-}COOH]$, whose CA mass spectrum[13] was compared with that of the $[C_2H_3O_2]^+$ ions obtained by collisional induced charge reversal of acetate anions, $[CH_3{-}COO]^-$[13,14] with helium. The latter result was interpreted[13] in terms of the formation of transient acyloxy cations, $[CH_3COO]^+$, in either a singlet or a triplet state. These undergo complete dissociation in the energy manifold and time frame ($\sim$0.1 μs) appropriate to the charge reversal experiment.[1]

Theoretical calculations[16,17] have been performed for the acyloxy cation, which as described above has escaped direct observation as a stable gas-phase species. The results indicate that the ion CH_3COO^+ may isomerize into its energetically more favorable cyclic dioxyryl form $[CH_3{-}{}^+\overline{C{-}O{-}O}]$. Nevertheless, decomposition into CH_3^+ and CO_2 was calculated to be exothermic but possibly via an energy barrier.

In addition to the two incompletely characterized stable isomers described above, nine more $[C_2H_3O_2]^+$ ions, depicted in Scheme I, may be expected to be stable observable species in the gas phase. These include the hydroxy-substituted oxiranyl and acetyl cations **2** and **4**, protonated glyoxal, **8**, the ion **9**, proposed to be generated[18] by dissociative $CH_3^\bullet$ loss from $[H{-}CO{-}OCH_2CH_3]^{\bullet+}$, and two carbon monoxide hydrogen bridged species, **10** and **11**. Although ions of the latter type have not yet been characterized in the gas

Scheme I

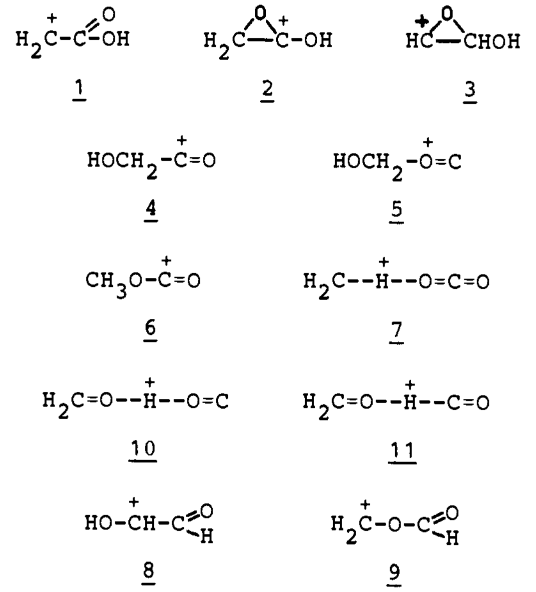

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Table I. Calculated Total Energies (Hartrees), Zero-Point Vibrational Energies (kcal/mol), and Relative Energies (kcal/mol) for Stable Isomers in the $C_2H_3O_2^+$ Potential Surface

structure	symmetry	SCF/ STO-3G	CASSCF4/ STO-3G	SCF/ 4-31G	SCF/ 6-31G*$_p$	SCF/6-31G*// 6-31G*$_{fs}$	CEPA2/6-31G*// 6-31G*$_{fs}$	ZPVE/ 3-21G	rel[a] energies
1	C_s	−223.8777	*b*	−226.4851	−226.8280				
2	C_s	−223.9383	−223.9992	−226.4877	−226.8568	−226.8564	−227.4841	32.6	20.5
3	C_1	−223.8946	*b*	*b*					
4	C_1	−223.9685	−224.0664	−226.5374	−226.8895	−226.8870	−227.5121	33.3[c]	3.6
5	C_1	−223.9478		−226.5500					
6	C_s	−223.9761	−224.0654	−226.5456	−226.9008	−226.8981	−227.5169	32.7[c]	0
7	C_{2v}	−223.8698	−223.9498	−226.5199	−226.8768	−226.8767	−227.4689	29.4	27.2
8	C_s	−223.9436	−224.0329	−226.5198	−226.8713	−226.8670	−227.4966	31.1	11.3
9	C_s	−223.9532	−224.0420	−226.5287	−226.8831	−226.8798	−227.5024	32.9	9.4
10	C_s	−223.9641	−224.0053	−226.5572	−226.9071	−226.9057	−227.5140	31.4[c]	0.7
11	C_s	−223.9676		−226.5516					

[a] The relative energies are for the CEPA2/6-31G*//6-31G*$_{fs}$ calculations including scaled (0.9) zero-point vibrational contributions.[31] [b] No local minimum at this level of theory (see text). [c] Calculated at the 4-31G level of theory (see text).

phase, a recent ab initio study on the related $[CH_3O_2]^+$ system predicts such ions to be quite stable.[19]

The aim of the present work was to establish which of the structures shown in Scheme I are predicted by high level ab initio molecular orbital theory calculations to exist as stable species in the gas phase and to compute their relative energies. The results of these calculations were used as a guide for the evaluation of the mass spectrometric experiments. These comprised heat of formation determinations and examination of unimolecular and collisional induced decompositions.

Theoretical Methods and Results

Standard LCAO–MO–SCF calculations were performed with the program GAMESS,[20] employing restricted Hartree–Fock (RHF) procedures.[21,22] Geometries were determined with gradient optimization procedures. Standard STO-3G,[23a] 4-31G,[23b] and 6-31G*[23c] basis sets were used.

In previous work (e.g., ref 8) we have employed the procedure of Radom et al.[7] to determine the final geometries to be used for single-point calculations.

However, at the SCF level or with small basis sets, problems have arisen with respect to the relationship between small cyclic ions and their ring-opened counterparts in, e.g., $[C_2H_3O]^+$[4] and $[C_2H_2O]^{\bullet+}$[24] isomeric ions. In the present investigation it was found that the SCF local minimum for isomer **1** disappeared when electron correlation was included. It was therefore decided to use correlated wave functions in the geometry optimization by using the CASSCF procedure[25] as implemented in the program GAMESS. CASSCF stands for the Complete Active Space Self Consistent Field procedure, and it is a special case of the well-known multi-configuration SCF (MCSCF) procedure.[26]

In the case of CASSCF calculations one selects an active orbital space which consists of occupied orbitals and unoccupied (virtual) orbitals. In our case the number of occupied and virtual orbitals is equal. Within this active space all excitations are allowed, so a full CI (configuration interaction) calculation is done for the active space chosen. The CASSCF procedure optimizes the orbitals, making possible gradient calculations which then can be used in geometry optimizations. In view of the expense of CASSCF calculations the small STO-3G basis set was used in the present work. The number of configurations in the CASSCF wave function increases rapidly with the number of active orbitals. Therefore only those orbitals which directly participate in isomerizations have been included in the active orbital set.

In order to obtain energies of comparable accuracy, the number and symmetries of the active orbitals were kept the same for all points on each potential energy surface. For the cations considered here there are two important correlation effects: (1) isomeric cations involving σ-bond breaking can only correctly be described by including two σ-orbitals into the orbital set;[27] (2) the C=O bond in, e.g., CO[28] and HCOOH[29] has been observed to be very sensitive to correlation effects in the π-orbital system due to the π–π* near-degeneracy effect. Therefore, all CASSCF calculations for the $[C_2H_3O_2]^+$ isomers were performed with four active orbitals, two σ-orbitals and two π-orbitals for conformations with C_s symmetry.

To combine the effects of correlation and basis set extension the following procedure was used: (1) All isomers were fully optimized at the SCF/STO-3G level (see Table I) and for selected isomers at the CASSCF/STO-3G level (Table I); (2) A number of isomers were partially, (p), geometry optimized at the SCF/6-31G* level, for only the heavy atom distances, angles, and dihedral angles. For isomers **7** and **10** the C–H and O–H distances, angles, and dihedral angles related to their hydrogen bridge were also optimized (the 6-31G*$_p$ column in Table I); (3) For the final geometries the heavy-atom distances, angles, and dihedral angles at the 6-31G*$_p$ level were corrected for correlation by adding the difference between the SCF/STO-3G and CASSCF/STO-3G results. These final structures, (fs), denoted as 6-31G*$_{fs}$ in Table I, were then used for single-point energy calculations at the SCF/6-31G* and coupled electron pair approximation CEPA2/6-31G* level,[30] denoted in Table I as respectively SCF/6-31G*/6-31G*$_{fs}$ and CEPA2/6-31G*//6-31G*$_{fs}$.

The relative energies given in the final column of Table I were obtained by correcting the CEPA2/6-31G* results for zero-point

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vibrational energies. The latter were obtained by performing geometry optimizations at the SCF/4-31G level (Table I), which in turn were used for calculating harmonic vibrational energies at the HF level with the split valence 3-21G basis.[31]

The structures displayed in the text refer to the 6-31G$^*_{fs}$ calculations, except for isomers **1** (6-31G$^*_{p}$), and **5** and **11** (4-31G), and **3** (STO-3G).

Throughout this paper, bond lengths are given in angstroms and bond angles in degrees. All energy comparisons refer to the relative energies shown in the last column of Table I.

Experimental Section

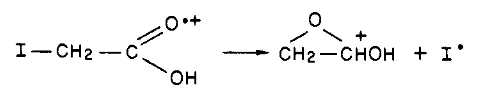
Collisional activation (CA) mass spectra and metastable peak observations were recorded on VG Analytical ZAB-2F mass spectrometers in Ottawa and Utrecht as described in ref 3. Appearance energies were measured with an apparatus comprising an electrostatic electron monochromator together with a quadrupole mass analyzer and minicomputer data system.[32,33] All compounds used were of research grade purity; this was particularly important because $[C_3H_7O]^+$, *m/z* 59 ions, present as an impurity or a mass spectrometer background contamination, give intense *m/z* 31 and 41 peaks in their CA mass spectra.

Results and Discussion

In order to correlate theory and experiment it has been customary to firmly establish the heats of formation of isomeric ions from appearance energy (AE) measurements and compare them with the relative energies resulting from calculations. However, as will be described later, the thermochemistry of $C_2H_3O_2^+$ ions proved less easy than expected to establish by experiment.

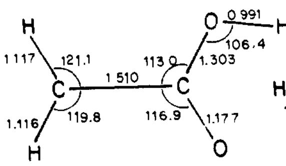
Ions **1**, **2**, and **3** will be discussed first.

The Ion C^+H_2COOH (1) and the Hydroxyoxiranyl Cations 2 and 3. The *m/z* 59 $C_2H_3O_2^+$ ions in the mass spectrum of ICH_2COOH may reasonably be proposed to have structure **1**, which would result from a simple, direct bond cleavage, or structure **2**, produced via an anchimerically assisted reaction[34]

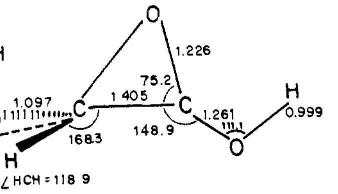


$I{-}CH_2{-}C(=O^{\bullet+}){-}OH \longrightarrow \overset{O^{+}}{CH_2{-}CHOH} + I^{\bullet}$

The optimized geometries of isomers **1**, **2**, and **3** are shown below for the highest levels of theory employed (see Table I). As shown in Table I, ion **1** was found not to exist in a potential well, but its ring-closed isomer, **2**, is a local minimum on the potential energy surface.



1



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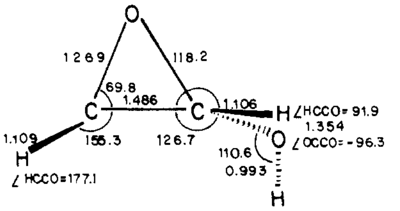

3

Similar observations have been reported for the analogous $[C_2H_3O]^+$ isomers $[C^+H_2CHO]$ and $\overline{CH_2{-}C^+HO}$ in that (1) all precursor molecules which could produce the methyleneformyl cation by direct bond cleavage yielded instead[3,35] the oxiranyl cation and (2) from ab initio calculations Radom et al.[4] concluded that, in contrast with the oxiranyl cation, $[C^+H_2CHO]$ is not a minimum on the $[C_2H_3O]^+$ potential energy surface.

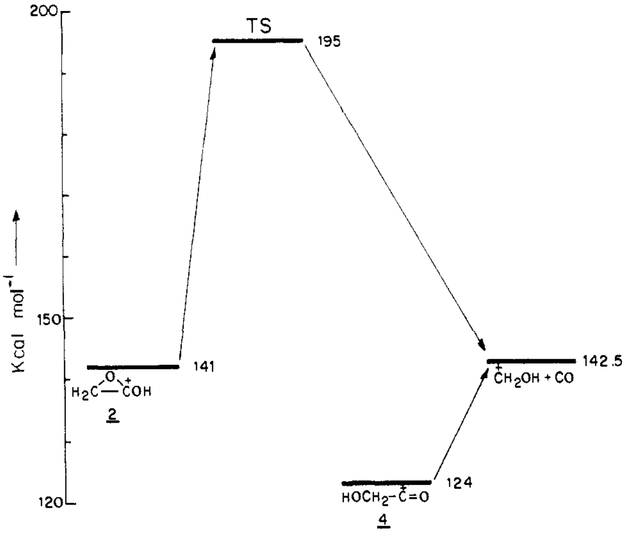

Figure 1. Energy diagram for the fragmentation $\overline{O{-}CH_2{-}C^+{-}OH}$, **2**, → $C^+H_2OH + CO$. $\Delta H_f^\circ(2)$ and $\Delta H_f^\circ(4)$ from experiment and theoretical calculation, respectively. Transition-state energy from a metastable peak appearance energy measurement;[57] product energies from ref 39.

The appearance energy (AE) of *m/z* 59, the base peak in the mass spectrum of ICH_2COOH, was 10.86 ± 0.05 eV, giving $\Delta H_f^\circ[C_2H_3O_2]^+ = 141 \pm 1$ kcal/mol ($\Delta H_f^\circ[ICH_2COOH] = -84 \pm 1$ kcal/mol,[36] $\Delta H_f^\circ[I] = 25.5$ kcal/mol[39]). This fragmentation is accompanied by a weak Gaussian type metastable peak; the kinetic energy release measured from the peak width at half-height, $T_{0.5}$, was only 6 meV, showing that the dissociation does not involve a reverse energy barrier[1] and that therefore the derived ΔH_f° corresponds to the production of an ion at or very close to its thermochemical threshold.

An estimate for $\Delta H_f^\circ(\mathbf{2})$ can be made by consideration of the effect of OH substitution at the charge bearing site in the oxiranyl cation, $\overline{CH_2{-}O{-}CH^+}$, whose heat of formation is well-established by both theoretical calculation and experiment,[3] as 215 ± 1 kcal/mol. The OH substitution effect can be estimated from $\Delta H_f^\circ[CH_2CH_2]^{\bullet+} = 255$ kcal/mol[39] and $\Delta H_f^\circ[CH_2CHOH]^{\bullet+} = 181$ kcal/mol.[40] Thus $\Delta H_f^\circ(\mathbf{2}) = 215 - 74 \simeq 141$ kcal/mol, no adjustment for ion size effect being necessary.[41]

On the basis of the above results, we propose that ion **2** is generated from ICH_2COOH at its thermochemical threshold. Its $\Delta H_f^\circ = 141 \pm 1$ kcal/mol will be used hereafter as the anchor point for the relative ionic heats of formation given in the last column of Table I.

Note that isomer **3** has an appreciably higher energy than **2** at the SCF/STO-3G level of computation. This could be predicted, this isomer being an oxiranyl cation having OH at a *noncharge-bearing site* and whose ΔH_f° would be ca. 36 kcal/mol above $\Delta H_f^\circ(\mathbf{2})$ on the basis of OH substitution effects.[42] However,

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[36] $\Delta H_f^\circ[ICH_2COOH]$ estimated by adding 19.5 ± 1 kcal/mol to $\Delta H_f^\circ[CH_3COOH] = -103.3$ kal/mol.[37] From Benson's additivity scheme[38] the effect of $-CH_3$ to $-CH_2I = +18.2$ kcal/mol; the difference in the ΔH_f° for $[CH_3COCH_3]$ and $[CH_3COCH_2I] = 20.7$ kcal/mol,[37] mean difference $= +19.5 \pm 1$ kcal/mol.

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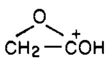
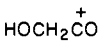
Table II. Collisional Activation Mass Spectra of $C_2H_3O_2^+$ Isomers[c]

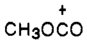


2



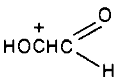
$HOCH_2\overset{+}{C}O$

4

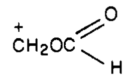


$CH_3O\overset{+}{C}O$

6



8



9

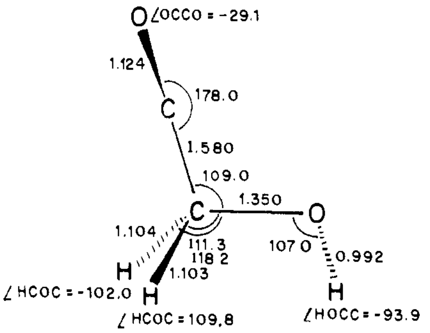
	designated ion structure				
m/z	**2**	**4**	**6**	**8**	**9**
12	50		6	7	1
13	120	1	12	21	3
14	325	2	39	46	8
15	37		(1000)		
16	12		7		
17	46				
18	11				
28	*a*	26	145	120[b]	19
29	1000	69	210	1000	125
30	345	26	59	320	39
31	(500)	(1000)		600	(1000)
40	70			25	
41	180	4		115	
42	340	5		57	1
44	160		410		7
45	800		63		
56	37		11	75	
58	95	9	46	440	1

[a] The CA mass spectrum also contains a broad unresolved signal at m/z 24–26; intensity ca. 50. [b] The CA mass spectrum also contains a broad unresolved signal at m/z 24–26; intensity ca. 15. [c] Peak heights, normalized to most intense peak = 1000. Parentheses refer to peaks having a contribution from a metastable decomposition.

it was found that at both SCF/4-31G and CASSCF4/STO-3G levels of theory that ion **3** is not a local minimum at the $[C_2H_3O_2]^+$ potential energy surface and that it rearranges into the open structure **8**.

The MI mass spectrum of ion **2** consists of an intense, broad, dished peak at m/z 31, $[CH_2OH]^+$, $T_{0.5}$ = 1230 meV, T_h (from the peak width across its summit) = 980 meV, showing that this fragmentation has a considerable reverse energy barrier.[43] The AE of this metastable peak was measured to be 13.2 ± 0.1 eV; this threshold energy leads to a transition-state energy of 195 kcal/mol and thus an energy barrier of ~54 kcal/mol exists for dissociation of **2** into $[CH_2OH]^+$ + CO. This is shown in Figure 1 together with ion **4**, $[HOCH_2—C^+{=}O]$, which dissociates into the same reaction products without a barrier (vide infra). Because of technical reasons it was impossible to locate the transition state at the CASSCF4/STO-3G level of theory.

The CA mass spectrum of **2** is given in Table II. The spectrum is in keeping with the proposed structure, but it is in poor agreement with that described by Bursey et al.,[13] who did not find the unimolecular process leading to m/z 31 but instead reported m/z 15 as (the only) metastable peak. The present observations were performed on ICH_2COOH samples of different origin, and results from both of our laboratories were in excellent agreement.



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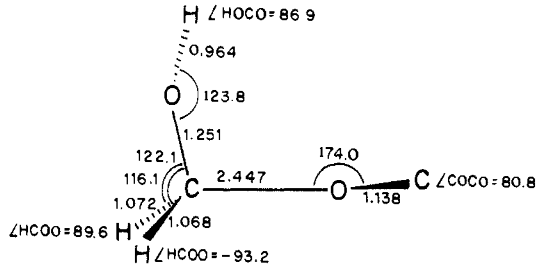

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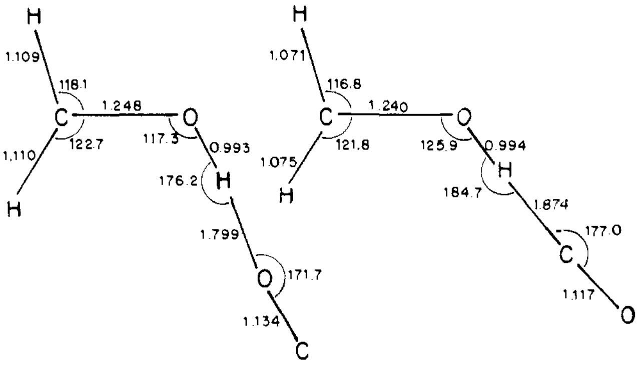
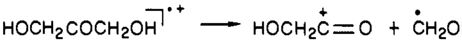


10

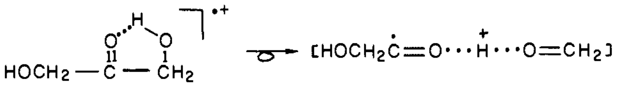
11

The Hydroxyacetyl Cation 4 and Ions 5, 10, and 11. These four ions are plausible reaction products of the ion–molecule reaction $[C^+H_2OH] + CO \rightarrow [C_2H_3O_2]^+$, which to our knowledge has not yet been studied. All four species, whose optimized geometries are shown below, represent minima on the $[C_2H_3O_2]^+$ potential energy surface. However, full CEPA2/6-31G* calculations were limited to those isomers, **4** and **10**, whose generation by dissociative ionization may a priori be expected. Using the experimentally derived $\Delta H_f°(\mathbf{2})$, 141 kcal/mol, and the calculated relative energies from Table I, the expected values for $\Delta H_f°(\mathbf{4})$ and $\Delta H_f°(\mathbf{10})$ are 124 and 121 kcal/mol, respectively. An estimate for $\Delta H_f°(\mathbf{4})$ can be made via an OH-substitution in the acetyl cation on the non-charge-bearing C-atom, whence $\Delta H_f°(\mathbf{4}) = 156^{44} - 36 = 120$ kcal/mol. For ion **10** no such estimation can be performed. The stabilization energy, 21.5 kcal/mol, of this hydrogen-bridged ion relative to the dissociation products $[C^+H_2OH]$ + CO ($\Delta H_f°$-($[CH_2OH]^+$ + [CO]) = 142.5 kcal/mol,[39] $\Delta H_f°(\mathbf{10})$ = 121 kcal/mol, see above) falls within the experimentally obtained[45a,b] range of stabilization energies for unsymmetrical proton bound dimers (20–30 kcal/mol). The m/z 59 $[C_2H_3O_2]^+$ ions in the mass spectrum of 1,3-dihydroxyacetone (2% of the base peak, m/z 31, $[C^+H_2OH]$) will have structure **4** if the dissociation reaction involves direct bond cleavage from the intact molecular ions:



$$HOCH_2COCH_2OH]^{\cdot+} \longrightarrow HOCH_2\overset{+}{C}{=}O + \overset{\bullet}{C}H_2OH$$

Alternatively, following the concept proposed by Morton,[46] the $CH_2OH^\bullet$ loss may also occur from molecular ions which have rearranged via an internal hydrogen bond shift and C–C bond fission into hydrogen-bridged radical cations



$$\rightarrow [HOCH_2\dot{C}{=}O\cdots\overset{+}{H}\cdots O{=}CH_2]$$

to yield ions **4** and **10** by subsequent loss of $\dot{C}H_2OH$. A combined

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experimental and computational study[47] on ionized glycolaldehyde—also an internally hydrogen bonded molecule—and where loss of CO yields the ylide ion $[CH_2OH_2]^{\bullet+}$,[6] is found to fragment via an isomerization into hydrogen-bridged ions of the type $[H—C{=}O\cdot\cdot H\cdot\cdot O{=}CH_2]^{\bullet+}$.

The MI mass spectrum of the $[C_2H_3O_2]^+$ ions from dihydroxyacetone consists of a single narrow Gaussian type peak at m/z 31, CH_2OH^+, $T_{0.5}$ = 6 meV, indicating the absence of any reverse energy barrier. The CA mass spectrum is wholly dominated by m/z 31 (Table II) and its fragmentation peaks at m/z 30–28. These features could readily be attributed to both ions **4** and **10**, but the minor peaks at m/z 42 and 41 indicate the presence of a C–C–O structure unit which is compatible with the generation of ions of structure **4**.

The AE of the m/z 59 ions was 11.24 ± 0.05 eV (average of several measurements), leading to $\Delta H_f°[C_2H_3O_2]^+ = 142 \pm 2$ kcal/mol (using $\Delta H_f°$(1,3-dihydroxyacetone) = −123 ± 2 kcal/mol, by additivity and assigning $C(H)_2(O)CO \equiv C(H)_2(O)(C) = -8.1$ kcal/mol; $\Delta H_f°[CH_2OH]^\bullet = -6.2$ kcal/mol[48]) some 20 kcal/mol above the estimated and computationally derived values for **4** and **10**.

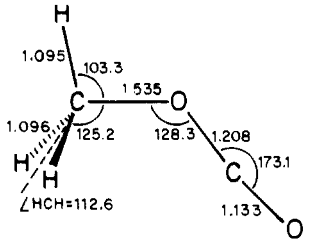
This energy (see Figure 1) is almost at the dissociation limit to $[C^+H_2OH]$ + CO. This measured high energy requirement for the generation of **4** and/or **10** is in line with the low abundance of m/z 59 in the mass spectrum of 1,3-dihydroxyacetone and the high abundance of m/z 31 therein and in the CA mass spectrum of m/z 59. The reason for the failure to observe the generation of the ions at the expected threshold energy is not known, but it should be noted that monohydroxyacetone (acetol) has been observed to behave similarly, i.e., the apparent $\Delta H_f°[CH_3—C^+{=}O]$ derived from AE measurements on the reaction

$$HOCH_2COCH_3 \rightarrow CH_3—C^+{=}O + \dot{C}H_2OH + e$$

was found to be 1 eV higher than that calculated for the threshold generation of the acetyl cation.[49]

Thus, although the characteristic MI and CA mass spectra of the dihydroxyacetone $[C_2H_3O_2]^+$ ion point to the formation of **4/10** ions, a firm structure assignment is not at present possible.

The Ions $CH_3O—C^+{=}O$ (6) and $CH_2—H^+—OCO$ (7). The calculated geometries of these two ions are as shown below. The methoxycarbonyl cation proved to be the thermodynamically most stable isomer (Table I), $\Delta H_f°$(**6**) = 120 kcal/mol. Ion **7** is calculated to have a $\Delta H_f°$ higher by 27 kcal/mol. It is closely related to **6** and can be considered as a methylene/CO_2 hydrogen-bridged ion. Such unconventional -C- -H- -O- hydrogen-bridged ions have recently been considered experimentally in ion–molecule reactions of, e.g., $[sec\text{-}C_3H_7]^+$ ions with H_2O[50] and CH_3OH.[51] The relationship of this type of H-bridged ion with conventionally σ-bonded species in open-shell distonic[5] ions like $[\text{ethylene}/H_2O]^{\bullet+}$,[8] $[\text{propene}/H_2O]^{\bullet+}$,[52] and $[\text{ketene}/H_2O]^{\bullet+}$[53] has been the subject of ab initio calculations, which show that, at least among these systems, barriers for interconversion are low. A variety of methylcarboxylates (all those shown in Table III) yield by direct bond cleavage a common $[C_2H_3O_2]^+$ ion which has MI and CA characteristics in keeping with structure **6**. The MI spectrum contains only m/z 15, CH_3^+, a Gaussian type peak with $T_{0.5}$ = 0.2 meV, indicating that the dissociation has no reverse energy barrier. Formation of CH_3^+ is the reaction of lowest energy requirement for ion **6** ($\Delta H_f°[CH_3]^+$ = 261 kcal/mol, $\Delta H_f°[CO_2]$ = −94 kcal/mol[39]), the product energies lying 47 kcal above the ion **6**.



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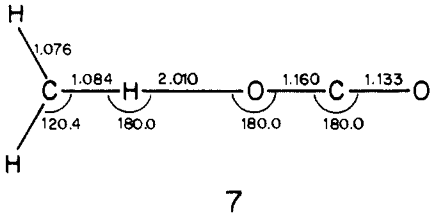

7

The CA mass spectrum (Table II) is in good agreement with that reported by Bursey et al.,[13] except that in the present work, a broad peak at m/z 30, overlapping m/z 29, was observed. It is noteworthy that in spite of the large internal energy range available to nonfragmenting $[CH_3OCO]^+$ ions, the low-energy $[CH_2OH]^+$ ion (m/z 31) is conspicuously absent and the formation requires only a simple rearrangement. The CA mass spectrum does contain an ion whose formation would require a rearrangement, namely m/z 45 $[COOH]^+$. Provided that ions **6** and **7** are able to interconvert prior to fragmentation, the presence of m/z 45 is easily accounted for ($\Delta H_f°[CO_2]^+ + [CH_3]^\bullet$ = 255 kcal/mol, and $\Delta H_f°[\ddot{C}H_2] + [HOCO]^+$ = 235 kcal/mol).

Note that is is unlikely that the CA mass spectrum of **7** could contain any structurally significant fragment ion other than those observed for $[CH_3OCO]^+$ and thus present experimental methods have not been able to identify the former ion. Appearance energy measurements were made for m/z 59 derived from a variety of methyl esters, and the results are presented in Table III. The $\Delta H_f°[C_2H_3O_2]^+$ values are significantly lower than those reported by Briggs and Shannon,[14] but they nevertheless range from 125 to 136 kcal/mol. For all the precursor molecules except methyl chloroformate, there are competing fragmentations of substantially lower energy requirement, ranging from 0.5 to 1.2 eV below the AE for m/z 59 ions. It is therefore possible that the majority of the $\Delta H_f°$(**6**) values suffer a competitive shift (ref 39, p 27).

Dimethyl carbonate has two competing fragmentations lower in energy by ca. 0.5 eV, namely to m/z 61 (AE = 10.94)[54] and m/z 62 (AE = 11.06 eV).[54] However, it was not possible unequivocally to identify the structure of the $[C,H_3,O]^\bullet$ neutral fragment[55] accompanying m/z 59 (see Table III) and so $\Delta H_f°$(**6**) from this molecule must be regarded as uncertain.

In the case of methyl chloroformate, m/z 59 is both base peak in the normal spectrum and the daughter ion of lowest energy requirement. This reaction is accompanied by an intense, broad, steepsided metastable peak (the only signal in the MI mass spectrum of $[ClCOOCH_3]^{\bullet+}$) having a very small narrow component on its summit. Both components are solely of unimolecular origin. Note that the metastably generated $[C_2H_3O_2]^+$ ions have a CA mass spectrum indistinguishable from their counterparts produced in the ion source, indicating that only the $[CH_3OCO]^+$ structure is present among low and high internal energy species. Thus the generation of **6** from ionized methyl chloroformate involves a reverse energy barrier; $\Delta H_f°$(**6**) derived from the AE measurements is therefore too high, but a reliable correction cannot be made. Thus, the calculated energy for the $[CH_3OCO]^+$ ion,

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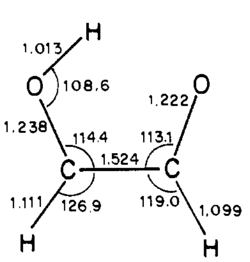
Table III. Appearance Energies and $\Delta H_\mathrm{f}^\circ$ Values for $[CH_3OC^+O]$ Ions

precursor molecule (M)	$\Delta H_\mathrm{f}^\circ[M]$ (kcal/mol)	AE m/z 59 ± 0.05 eV	neutral product(s) and $\Delta H_\mathrm{f}^\circ$ values (kcal/mol)		$\Delta H_\mathrm{f}^\circ[C_2H_3O_2]^+$ (kcal/mol)
$(CH_3O)_2CO$	-136^{38}	11.50	$CH_3O^\bullet$ ($^\bullet CH_2OH$)	4.2^{48} $(-6.2^{48})^e$	125
$BrCH_2COOCH_3$	$-89^a \pm 2$	11.16	$^\bullet CH_2Br$	41.5^{48}	127 ± 2
$ClCH_2COOCH_3$	$-99^b \pm 2.5$ $(-104)^c$	11.10	$^\bullet CH_2Cl$	28.3^{48}	128 ± 2.5 (124)
$ClCOOCH_3$	-104^d	11.24	$^\bullet Cl$	29.1^{39}	126
CH_3COOCH_3	-98.0^{37}	11.32	$^\bullet CH_3$	35^{48}	128
cy $C_3H_5COOCH_3$	-72.4^{38}	10.56	$\overset{\bullet}{\overline{CH_2CHCH_2}}$	40^{48}	131
$CH_3CH_2COOCH_3$	-103.8^{38}	11.42	$CH_3CH_2^\bullet$	28^{48}	132
$HOCH_2COOCH_3$	-133.0^{38}	11.38	$^\bullet CH_2OH$	-6.2^{48}	136
$CH_3COCOOCH_3$	-121^{38}	11.50	$^\bullet CH_3 + CO$	$(-26.4)^{39}$	136

[a] From $\Delta H_\mathrm{f}^\circ[CH_3COOCH_3] = -98.0$ kcal/mol,[37] $\Delta H_\mathrm{f}^\circ[BrCH_2COCH_3] = -43.3 \pm 2^{37}$ kcal/mol, and $\Delta H_\mathrm{f}^\circ[CH_3COCH_3] = -52.0$ kcal/mol.[37] [b] From $\Delta H_\mathrm{f}^\circ[ClCH_2COOH] - \Delta H_\mathrm{f}^\circ[CH_3COOH] = -0.7 \pm 2.5$.[37] [c] From $\Delta H_\mathrm{f}^\circ[CH_3COOCH_3]^{37}$ and assuming $C-(Cl)(H)_2(CO) = C-(Cl)(H)_2(C) = -16.5$ kcal/mol,[38] whereas $C-(H)_3(CO) = -10.1$ kcal/mol;[38] the error in this assumption is uncertain. [d] Using $\Delta H_\mathrm{f}^\circ[CH_3COCl] = -58.0$ kcal/mol[37] and $\Delta H_\mathrm{f}^\circ[CH_3COOCH_3] - \Delta H_\mathrm{f}^\circ[CH_3COCH_3] = 98.0-52.0 = -46$ kcal/mol. Whence $\Delta H_\mathrm{f}^\circ[CH_3OCOCl] = -104$ kcal/mol. [e] There is no metastable peak for this process and so the assumed neutral structure cannot be tested by examining the collision-induced dissociative ionization mass spectrum of the neutral product.[56]

120 kcal/mol (Table I), is consistent with the above results.

The Ions HO—C$^+$H—C(=O)—H (8) and H$_2$C$^+$—O—C(=O)—H (9). The geometries of these ions are as shown below.



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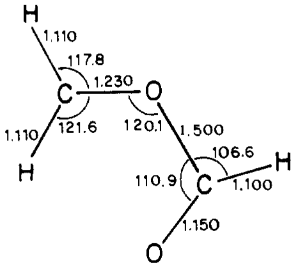

9

Ion **8** may reasonably be expected to be generated by the gas-phase protonation of glyoxal, HCOHCO. The CA mass spectrum of the m/z 59 ions thus generated (Table II) is in keeping with ions of structure **8**. The MI mass spectrum shows a single very weak signal at m/z 31, $[C^+H_2OH]$, with $T_{0.5} = 140$ meV. This indicates that interconversion of ions **8** and **4**, via a 1,2 H-shift, is not a facile process. This is corroborated by the fact that reactions observed under collision conditions, which are thermochemically more energy demanding (e.g., the formations of m/z 29, $[H—C^+=O]$ and m/z 58, $[HCOHCO]^{\bullet+}$), compete favorably with the formation of m/z 31.

The theoretically derived heat of formation of the ion, 132 kcal/mol, cannot be compared with an experimental value since the proton affinity of glyoxal has not been reported.

Ion **9** has been proposed to be formed by loss of $CH_3^\bullet$ from ionized ethyl formate, in the normal mass spectrum of which is ca. 1% of the base peak[18] (m/z 31). Labeling experiments clearly showed[18,56] that the $CH_3^\bullet$ group is lost without prior H-atom exchange. The reported AE value for this ion, 11.5 eV,[56] could not be repeated by ourselves, a limiting value of ≤11.8 eV being obtained because the weak peak approached the energy axis asymptotically. This, together with $\Delta H_\mathrm{f}^\circ[HCOOCH_2CH_3] = -93.5$ kcal/mol[38] and $\Delta H_\mathrm{f}^\circ[CH_3^\bullet] = 35$ kcal/mol,[48] gives $\Delta H_\mathrm{f}^\circ(\mathbf{9}) \leq 144$ kcal/mol, some 15 kcal/mol above the calculated value (Table I). The MI mass spectrum contains a single Gaussian-type peak, m/z 31, $[CH_2OH]^+$, $T_{0.5} = 18$ meV. The CA mass spectrum of this ion (Table II) is similar to that for ion **4**, except for the presence of m/z 44 $[CO_2]^{\bullet+}$ in the former. This difference, the much smaller kinetic energy release for **4** → m/z 31, $T_{0.5} = 6$ meV, and the above labeling experiments lead us to propose that the ion derived from ethyl formate has indeed structure **9**.

In summary, theoretical calculations have been used to discover which of the eleven considered $C_2H_3O_2^+$ isomers exist in potential wells and to estimate the relative enthalpies of the seven stable species. Experimental observations on the hydroxyoxiranyl cation, **2**, and the methoxycarbonyl cation, **6**, agree satisfactorily with the calculations. Of the five remaining isomeric ions predicted by theory to be stable species, only protonated glyoxal, **8**, was soundly characterized by experiment, but tentative identifications of isomers **4** and **7** were also proposed. The dearth of reliable experimental measurements of $\Delta H_\mathrm{f}^\circ$ values for more than two of the isomers does not permit a critical appraisal of the calculated relative energies.

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Registry No. **1**, 72063-59-3; **2**, 104598-62-1; **3**, 104598-63-2; **4**, 51583-45-0; **5**, 104598-64-3; **6**, 24434-00-2; **8**, 61134-51-8; **9**, 104598-65-4; $(CH_3O)_2CO$, 616-38-6; $BrCH_2COOCH_3$, 96-32-2; $ClCH_2COOCH_3$, 96-34-4; $ClCOOCH_3$, 79-22-1; CH_3COOCH_3, 79-20-9; c-$C_3H_5COOCH_3$, 2868-37-3; $CH_3CH_2COOCH_3$, 554-12-1; $HOCH_2COOCH_3$, 96-35-5; $CH_3COCOOCH_3$, 600-22-6; CH_3^+, 14531-53-4; $HCHO{\cdot}H^+$, 18682-95-6; CO, 630-08-0; CO_2, 124-38-9.

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