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An Experimental and Theoretical Study of Ionized Hydroxyacetone: A Stable, Hydrogen-Bridged Radical Cation

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Abstract: Ion–molecule reactions and collision-activated dissociation experiments were used to examine the structure of the long-lived, low-energy molecular ion of hydroxyacetone $[CH_3C(O)CH_2OH]^{\bullet+}$ (**1**) in a dual-cell Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR). It is demonstrated that a significant proportion of the nonfragmenting ions have a noncovalent, hydrogen-bridged structure, most likely $[CH_3C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**2**). This hydrogen-bridged ion undergoes reactions which are unique for a radical cation and which can best be described as solvent switching reactions: neutral reagents replace the acetyl radical in the ion. High-level *ab initio* molecular orbital calculations up to the MP2/6-31G**//6-31G**+ZPVE level of theory were performed to study the potential energy surface of the $[C_3H_6O_2]^{\bullet+}$ isomers. The hydrogen-bridged species **2** was found to be more stable by 10.2 kcal/mol than the covalently bonded, ionized hydroxyacetone **1**. The enol isomers of ionized hydroxyacetone were calculated to be the most stable of all the structures studied, but these ions were not observed experimentally. The importance of three other hydrogen-bridged radical cations, $[CH_3C(H){=}O\cdots H\cdots O{=}CH]^{\bullet+}$ (**3**), $[CH_2{=}C(H)O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**4**), and $[CH_3C(O)\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**5**), is discussed.

Introduction

During the past 10 years, hydrogen-bridged radical cations have been proposed as intermediates in the isomerization/dissociation reactions of a wide range of organic radical cations.[1–15] Although high-level *ab initio* molecular orbital calculations indicate that many hydrogen-bridged $\text{-}O\cdots H\cdots O\text{-}$,[4–10] $\text{-}C\cdots H\cdots O\text{-}$,[11] and $\text{-}N\cdots H\cdots O\text{-}$[12–14] radical cations correspond to an energy minimum, not much experimental evidence exists to support such long-lived species. In fact, it has been stated recently that unambiguous evidence is not available for the existence of hydrogen-bridged radical cations either as intermediates or as products of gas-phase reactions.[5] It should be noted, however, that most of the work carried out to study these ions has been based on the investigation of dissociation reactions of conventional (covalently bound) radical cations assumed to decompose via a hydrogen-bridged structure. These studies can provide only indirect evidence for the transient existence of a hydrogen-bridged intermediate.

Theoretical calculations are well-suited for the study of gas-phase ions,[16,17] and the combination with mass spectrometry experiments has led to the identification of many unconventional and previously unknown radical cations. Calculations yield information about reaction energetics and mechanisms and thereby help to evaluate the importance of possible isomerization processes and the relative stabilities of different isomeric structures. Especially in studies of hydrogen-bridged radical cations, *ab initio* molecular orbital calculations have proved to be invaluable. For example, calculations have been used to show that these structures can correspond to a potential energy minimum. Geometry optimizations using split-valence basis sets and energy calculations including polarization functions and electron correlation have been shown to give reliable results for radical cations.[3,10,12,18]

Hydrogen-bridged radical cations have been proposed to play an important role in the unimolecular chemistry of certain $C_3H_6O_2^{\bullet+}$ ions.[3,10,15,20–23] The ion $[CH_3C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**2**) is a potential intermediate in the dissociation of metastable ionized methyl acetate $[CH_3C(O)OCH_3]^{\bullet+}$ (**6**).[3,10] This rearrangement was suggested, on the basis of calculations, first to yield a distonic ion $[CH_3C(OH)OCH_2]^{\bullet+}$ (**7**), followed by isomerization to form $[CH_3C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**2**), which dissociates to yield CH_3CO^+ and $^{\bullet}CH_2OH$ (Scheme I). Recent experimental work[19] has revealed that the *low-energy, long-*

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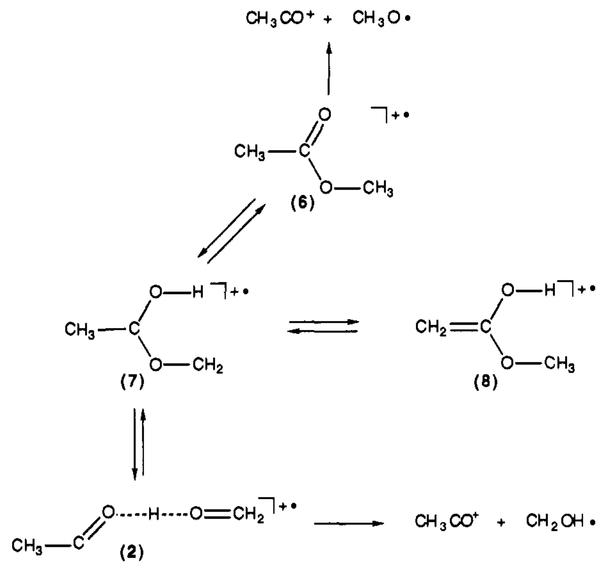
Scheme I



lived methyl acetate ions indeed isomerize to the distonic ion $[CH_3C(OH)OCH_2]^{\bullet+}$ (**7**). This ion, however, is unstable toward further isomerization to the enol form $[CH_2{=}C(OH)OCH_3]^{\bullet+}$ (**8**) (Scheme I). The distonic ion **7** and the enol form **8** have been calculated to be significantly lower in energy than the keto isomer.[3,10] No experimental evidence has been found for the generation of the hydrogen-bridged structure **2** from the nonfragmenting methyl acetate radical cation.[19]

Another $C_3H_6O_2^{\bullet+}$ ion, the hydroxyacetone radical cation $[CH_3C(O)CH_2OH]^{\bullet+}$ (**1**), shows interesting dissociation behavior[15,20,23] which also has been interpreted on the basis of hydrogen-bridged radical cation intermediates. The metastable molecular ion of hydroxyacetone yields two fragment ions, $[CH_3CO]^+$ (m/z 43) and $[CH_3CHOH]^+$ (m/z 45; the abundance ratio m/z 43: m/z 45 is 1:13). Results obtained upon examination of the dissociation products of partially isotopically labeled hydroxyacetone molecular ions have been rationalized[15,20,23] on the basis of isomerization of the molecular ion via the structure $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**) to the H-bridged species $[CH_2{=}C(H)O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**4**). The ion **4** was suggested to further isomerize to the hydrogen-bridged radical cation $[CH_3C(H){=}O{\cdots}H{\cdots}O{=}CH]^{\bullet+}$ (**3**), which then dissociates to yield CH_3CHOH^+ and $CHO^\bullet$ (Scheme II). It was also proposed that there may be no communication between the potential energy surfaces of the methyl acetate radical cation and the hydroxyacetone radical cation and, therefore, no common intermediates. The hydroxyacetone ion does not isomerize to the more stable enol tautomers $[CH_2{=}C(OH)CH_2OH]^{\bullet+}$ (**9**) and $[CH_3C(OH){=}CHOH]^{\bullet+}$ (**10**) prior to or during dissociation.[24] Further, ionized methyl acetate and its distonic and enol forms (**6–8**) apparently do not interconvert with the hydroxyacetone radical cation **1**.[20-22]

The interesting findings discussed above for the internally excited, ionized hydroxyacetone inspired the present study. In order to provide complementary information for this intriguing system, the *long-lived, low-energy* radical cation of hydroxyacetone (lifetime > 300 ms) was characterized by using a combination of ion–molecule reactions, collisional activation, and *ab initio* molecular orbital calculations. It is demonstrated that the long-lived ion partially isomerizes to a hydrogen-bridged radical cation, most likely the ion $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**) (Scheme III). The ion $[CH_2{=}C(H)O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**4**), which has been proposed to be formed[15,20,23] from the internally activated (e.g., metastable) molecular ions of hydroxyacetone, is not generated from the long-lived, low-energy ions. Instead, further isomerization of some of the ions **2** formed from **1** yields another H-bridged radical cation: $[CH_3C(H){=}O{\cdots}H{\cdots}O{=}CH]^{\bullet+}$ (**3**) (Scheme III). This ion is calculated to be 13.5 kcal/mol more stable than the ionized, covalently bonded hydroxyacetone and 3.3 kcal/mol more stable than the hydrogen-bridged radical cation $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**). The bimolecular reactions observed for these two hydrogen-bridged ions (**2** and **3**) are quite unique for a radical cation and differ considerably from those of isomeric covalently bonded radical cations, e.g., the enol form of ionized methyl acetate.[19]

Experimental and Theoretical Methods

All the experiments were carried out using a Fourier-transform ion cyclotron resonance mass spectrometer (Extrel Model 2001 FT/MS system). The reaction chamber consists of two identical, cubic 2-in. cells, and it is placed collinearly with a magnetic field produced by a 3-T superconducting magnet operated at 2.3 T. Each cell is independently pumped with a turbomolecular pump (Balzars TPU 330). The base pressure in each cell is less than 1×10^{-9} Torr, as measured by an ionization gauge in each side of the differentially pumped vacuum chamber. The ions were trapped in the magnetic field by applying a small positive voltage (+2 V) to the trapping plates of the cell. Reagents were introduced into the instrument by using either Extrel FT/MS heated single batch inlet systems equipped with leak valves or a pulsed valve inlet system. All the samples were obtained commercially and used as received.

The radical cation of hydroxyacetone was generated by electron ionization or by charge exchange using $CS_2^{\bullet+}$ reagent ions (ionization energy (IE) of CS_2 is 10.07 eV[25] and that of $CH_3C(O)CH_2OH$ is 10.0 eV[24]). The electron energy (20–75 V), filament current (2–10 μA), and ionization time (5–100 ms) were optimized separately for each experiment. After ionization, the ions were transferred into the other side of the dual cell through a 2-mm hole in the center of the common wall (conductance limit) by grounding this wall for 100 μs. The ions were then collisionally cooled by pulsing a relatively high pressure of argon into the cell. The radical cation of hydroxyacetone (m/z 74) was isolated by ejecting all the other ions from the cell by using the stored waveform inverse Fourier transform excitation method (Extrel FTMS SWIFT Module),[26] and/or by applying single frequency pulses to the excitation cell plates. The isolated molecular ion was allowed to react with the desired neutral reagent for a variable time period.

The nominal sample pressures were 1.0×10^{-7}–1.5×10^{-7} Torr, except for cyclohexanone, which was used at a nominal pressure of 6.0×10^{-8} Torr. The rate constants of the bimolecular reactions were calculated from the slope of the logarithm of the relative abundance of the reactant ion as a function of time. The pressure readings were corrected for the sensitivity of the ion gauge toward each of the neutral molecules studied.[27a] The ionization gauges were also calibrated for each neutral reagent by using common procedures based on well-characterized reactions with known rates;[27b] this correction was necessary because of the pressure gradient between the dual cell and the ion gauge. The precision of the rate measurements is better than 10%, and the accuracy is estimated to be better than ±50%.

For collision-activated dissociation (CAD) experiments, argon instead of an organic reagent was introduced through a leak valve into the second cell (a nominal pressure of 1.2×10^{-7} Torr). Instead of argon being pulsed into the cell in order to cool the ions, the ions were allowed to collide for a relatively long time period (1 s) with the argon present in the cell. The isolated ions were accelerated to a preselected final kinetic energy[28] by using an on-resonance radio frequency (rf) pulse. The final radius, and hence the final kinetic energy of the ions, is determined by the duration of the excitation pulse. Grosshans and Marshall[29] have shown that the laboratory kinetic energy of the ions in FT-ICR is about half the value computed according to the infinite parallel plate approximation, $E_{\mathrm{ion}} = q^2V^2t^2/8md^2$, where q is the ionic charge, V is the amplitude

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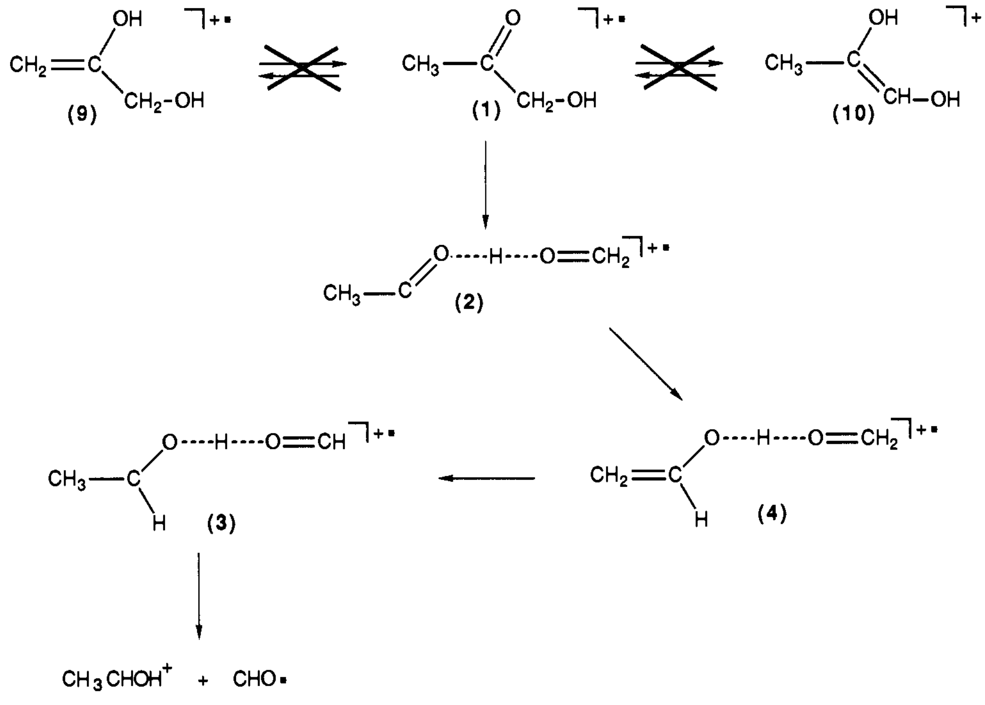
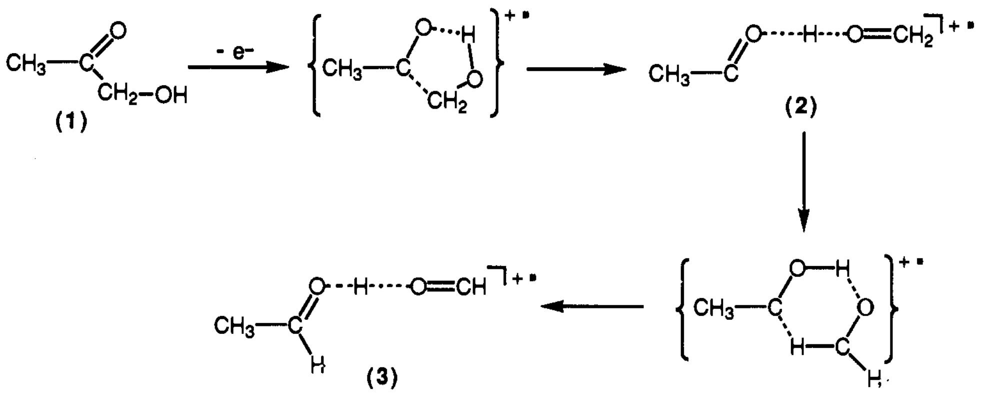
Scheme II



Scheme III



of the rf excitation pulse, *t* is the duration of the rf pulse, *m* is the ionic mass, and *d* is the distance between the excitation plates. By varying the duration of the excitation pulse, dissociation products for different estimated laboratory kinetic energies (12–200 eV) were measured. A time period of 100 ms was allowed for collisions of the accelerated ions with the argon target gas.

All the spectra shown are an average of at least 15 acquisitions which were recorded by taking 32K data points per scan at a digitizer rate of 5.3 MHz. The excitation sweep used for detection (chirp detection) had a bandwidth of 2.7 MHz, an amplitude of 124 V_{p-p}, and a sweep rate of 3.0 kHz/μs. The spectra were subjected to one zero fill prior to Fourier transformation.

Standard *ab initio* molecular orbital calculations were performed with the GAUSSIAN 90[30] and GAUSSIAN 92[31] series of programs employing spin-unrestricted Hartree–Fock (UHF) procedures[32] (Convex C3840 and SGI R4000 computers). Optimized geometries, harmonic frequencies, and zero-point vibrational energies (ZPVE) were calculated up to the 6-31G** basis set. The zero-point vibrational energy correction is necessary because of finite nuclear motion, even at low temperatures. Single-point energies for the 6-31G** geometries were obtained by including electron correlation through the use of Møller–Plesset perturbation calculations carried out to second order (MP2/6-31G**//6-31G**). The force constant matrices for the stationary points were checked to have the correct number of negative eigenvalues (zero for equilibrium structures and one for transition structures). Since Hartree–Fock calculations are known[33] to overestimate the vibrational frequencies by 10–15%, the zero-point energies were scaled by a factor of 0.9.

Results

Ion–molecule reactions and CAD experiments were carried out in order to examine the structure of the long-lived, low-energy molecular ion of hydroxyacetone. The molecular ion (m/z 74) was generated in one side of the dual-cell reaction chamber by electron ionization or by charge transfer using the $CS_2^{\bullet+}$ reagent ion, transferred into the other side of the cell, collisionally relaxed, and isolated. The ions had a lifetime of at least 300 ms prior to reactions. For ion–molecule reaction studies, the isolated ions were allowed to react with a neutral reagent for a variable period of time in order to determine the branching ratios of the products and the rate constant for each reaction. The product distributions and reaction efficiencies (observed reaction rate/collision rate[27c]) are given in Table I. For CAD, the isolated ions were accelerated

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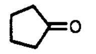
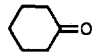
Table I. Ion–Molecule Reaction Rates and Primary Product Ions of Ionized Hydroxyacetone (m/z 74) Generated by Electron Impact

neutral reagent	MW	PA[a] (kcal/mol)	IE[b] (eV)	k[c]	$k_{\text{collision}}$[d]	k_{eff}[e]	product ions m/z	product ions relative intensity	reaction
CH_3CH_2CHO	58	189.6	10.0	0.7	2.3	0.3	89	100	replacement of $CH_3CO^•$
$(CD_3)_2CO$	64	197.0[f]	9.7[f]	1.5	2.6	0.6	65	70	H^+ transfer
							95	30	replacement of $CH_3CO^•$
	84	198.8	9.3	1.7	2.5	0.7	84	10	e^- transfer
							85	40	H^+ transfer
							115	50	replacement of $CH_3CO^•$
$C_2H_5COC_2H_5$	86	201.4	9.3	1.6	2.4	0.7	86	5	e^- transfer
							87	83	H^+ transfer
							117	12	replacement of $CH_3CO^•$
	98	201.0	9.1	2.7	2.5	1.1	98	14	e^- transfer
							99	76	H^+ transfer
							129	10	replacement of $CH_3CO^•$
CD_3OD	36	181.9[f]	10.9[f]	0.4	1.9	0.2	67	100	replacement of $CH_3CO^•$
$(CH_3)_2CHOH$	60	196.0	10.1	1.0	1.8	0.6	61	45	H^+ transfer
							91	55	replacement of $CH_3CO^•$
CH_3SSCH_3	94	196.0	8.0	1.0	1.0	0.5	94	93	e^- transfer
							95	7	H^+ transfer
							139	small	replacement of $CHO^•$
CH_3CH_2I	156	176.0	9.3	0.8	1.6	0.5	75	15	H abstraction
							156	75	e^- transfer
							201	10	replacement of $CHO^•$
CD_3CD_2I	161	176.0[f]	9.3[f]	0.7	1.6	0.4	76	7	D abstraction
							161	88	e^- transfer
							206	5	replacement of $CHO^•$
$CH_2{=}CHCH_2I$	168	not known	9.3	1.0	1.5	0.7	75	6	H abstraction
							168	68	e^- transfer
							169	20	H^+ transfer
							213	6	replacement of $CHO^•$
$(CH_3)_3CI$	184	not known	9.0	0.8	1.7	0.5	57	60	$C_4H_9^+$
							75	20	H abstraction
							184	20	e^- transfer
							229	small	replacement of $CHO^•$

[a] Proton affinity values from ref 25. [b] Ionization energy values from ref 25. [c] Rate constant, $\times 10^{-9}$ cm^3 s^{-1}. [d] Collision rate, $\times 10^{-9}$ cm^3 s^{-1}, obtained according to ref 27c. [e] Efficiency = $k/k_{\text{collision}}$. [f] Value for the corresponding undeuterated reagent.

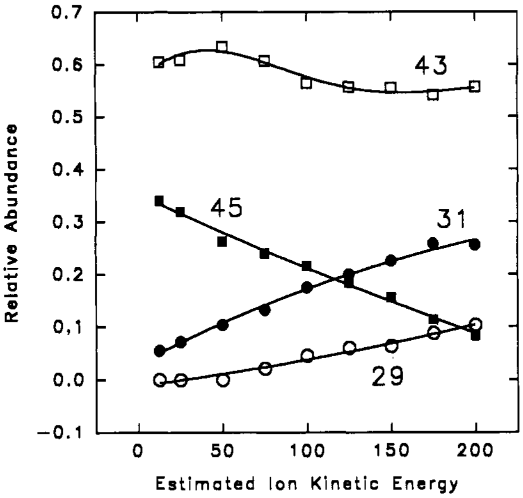


Figure 1. Collisional activation of the molecular ion of hydroxyacetone (m/z 74). The reaction time was 100 ms, and argon gas was used as the collision target at a nominal pressure of 1.2 × 10^{-7} Torr.

to a selected final laboratory kinetic energy (12–200 eV) and allowed to collide with argon. The relative fragment ion abundances vs laboratory kinetic energy are shown in Figure 1.

Ab initio molecular orbital calculations were carried out to evaluate the potential energy surface of the different $[C_3H_6O_2]^{•+}$ isomers. Several hydrogen-bridged structures were investigated and found to be stable; however, the two enol forms of the hydroxyacetone radical cation are the most stable out of all the structures studied here. The calculated energies are shown in Table II (total energies are in hartrees and relative energies in kcal/mol). All the structures shown are equilibrium structures, with the exception of the conformer of the conventional, covalently bonded ionized hydroxyacetone with the hydroxylic hydrogen pointing toward carbonyl oxygen (**1′**). The 6-31G** optimized geometries of the different $[C_3H_6O_2]^{•+}$ structures studied are given in Figure 2.

Discussion

Dissociation Reactions. Collision-activated dissociation (CAD) of the long-lived (lifetime > 300 ms) hydroxyacetone radical cation (m/z 74) yields several fragment ions: CHO^+ (m/z 29), CH_2OH^+ (m/z 31), CH_3CO^+ (m/z 43), and CH_3CHOH^+ (m/z 45) (Figure 1). The product distribution obtained is similar to that reported earlier for the short-lived molecular ion (microsecond lifetime prior to CAD).[24]

The fragment ion CH_3CO^+ is dominant at all energies (Figure 1). This stable ion arises by a direct bond cleavage either in the covalently bonded molecular ion or possibly in the hydrogen-bridged ion $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{•+}$ (**2**), as suggested[24] earlier (Scheme IV). At higher energies, the ions **1** and/or **2** yield another fragment ion: CH_2OH^+ (see Figure 1 and Scheme IV).

The fragment ion CH_3CHOH^+ (m/z 45) is abundant only at low energies. This finding suggests that the ion CH_3CHOH^+ arises from a rearrangement reaction which at high energies cannot compete with energetically less favorable but faster direct bond cleavages (e.g., CH_3CO^+ formation). The ion CH_3CHOH^+ is probably generated via isomerization of the molecular ion to the earlier proposed[23] hydrogen-bridged structure $[CH_3C(H){=}O{\cdots}H{\cdots}O{=}CH]^{•+}$ (**3**). The hydrogen bond to CH_3CHO is stronger than that to $CHO^•$ (CH_3CHO, PA = 187 kcal/mol; CHO, PA(O) = 146 kcal/mol);[25] hence, the hydrogen bond expected to break upon dissociation of **3** is the H–(OCH) bond to yield CH_3CHOH^+ (Scheme IV). The ion CHO^+ (m/z 29) may, at least partially, arise from dissociation of **3**. However, most of the ions CHO^+ are probably generated by further dissociation of other fragment ions (e.g., $CH_2OH^+ \rightarrow CHO^+ + H_2$).

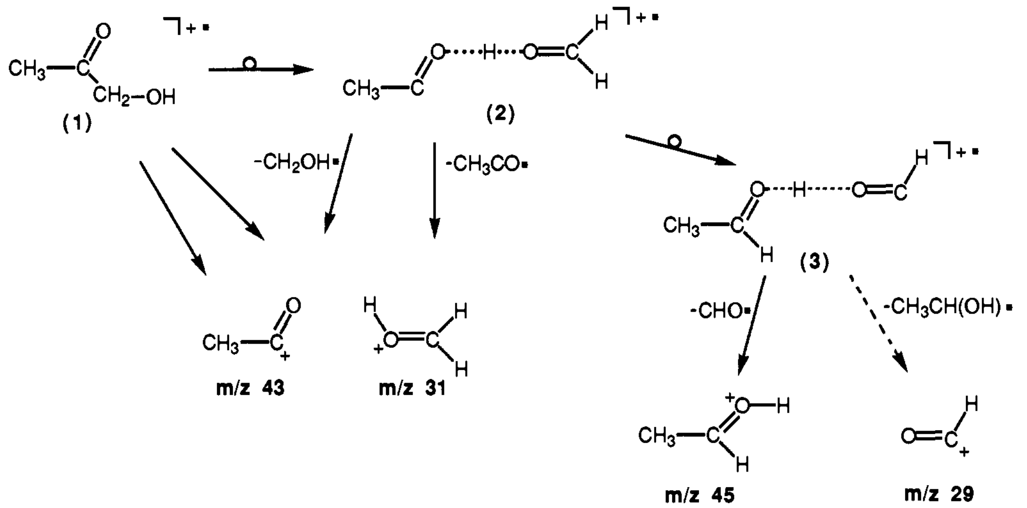
The results discussed above do not provide evidence for the formation of either one of the hydrogen-bridged species [$CH_2{=}C$-

Table II. Calculated Total Energies (hartrees), Relative Energies in Parentheses (kcal/mol), Zero-Point Vibrational Energies (ZPVE, in kcal/mol), and Final Relative Energies (kcal/mol) of the $[C_3H_6O_2]^{\bullet+}$ Structures

	basis set					
compound	3-21G	6-31G	6-31G**	MP2/6-31G**/ /6-31G**	ZPVE[a] (6-31G**)	MP2/6-31G**/ /6-31G**+ZPVE
$CH_3C(O)CH_2OH^{\bullet+}$ (**1**)	−265.010 86 (0)	−266.379 35 (0)	−266.516 02 (0)	−267.234 82 (0)	52.91	0.0
$CH_3C(O)CH_2OH^{\bullet+}$ (**1′**, TS)	−264.994 89 (10.1)	−266.362 62 (10.5)	−266.501 98 (8.8)	−267.222 47 (7.7)	52.42	7.3
$[CH_3C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**2**)	−265.014 72 (−2.4)	−266.373 32 (3.8)	−266.514 13 (1.2)	−267.248 76 (−8.8)	51.46	−10.2
$[CH_3C(H){=}O\cdots H\cdots O{=}CH]^{\bullet+}$ (**3**)	−265.015 79 (−3.1)	−266.377 10 (1.4)	−266.519 25 (−2.0)	−267.253 03 (−11.4)	50.88	−13.5
$[CH_2{=}C(H)O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**4**)	−265.029 55 (−11.7)	−266.393 58 (−8.9)	−266.530 41 (−9.0)	−267.260 84 (−16.3)	51.73	−17.5
$[CH_3C(O)\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**5**)	−264.998 07 (8.1)	−266.364 83 (9.1)	−266.499 90 (10.1)	−267.216 27 (11.6)	49.98	8.7
$[CH_3C(O)OCH_3]^{\bullet+}$ (**6**)	−265.039 75 (−18.1)	−266.391 78 (−7.8)	−266.533 22 (−10.8)	−267.248 98 (−8.9)	53.48	−8.3
$[CH_3C(OH)OCH_2]^{\bullet+}$ (**7**, syn)	−265.042 79 (−20.0)	−266.394 64 (−9.6)	−266.540 61 (−15.4)	−267.271 40 (−23.0)	53.21	−22.7
$[CH_3C(OH)OCH_2]^{\bullet+}$ (**7**, anti)	−265.036 90 (−16.3)	−266.389 15 (−6.1)	−266.537 28 (−13.4)	−267.268 05 (−20.9)	52.98	−20.8
$[CH_2{=}C(OH)CH_2OH]^{\bullet+}$ (**9**)	−265.037 87 (−16.9)	−266.394 64 (−9.6)	−266.541 35 (15.9)	−267.272 43 (−23.6)	54.18	−22.3
$[CH_3C(OH){=}CHOH]^{\bullet+}$ (**10**)	−265.053 72 (−26.9)	−266.420 97 (−26.1)	−266.561 76 (−28.7)	−267.303 48 (−43.1)	54.78	−41.2

[a] Scaled by a factor of 0.9.

Scheme IV



$(H)O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**4**) or $[CH_3C(O)\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**5**), although these structures cannot be ruled out on the basis of the CAD data alone. However, both of these ions would be expected to yield fragment ions of *m/z* 44 ($CH_2{=}CHOH^{\bullet+}$ and $CH_3CHO^{\bullet+}$, respectively) and *m/z* 30 (CH_2O). These fragment ions were not observed at any of the several collision energies studied.

Ion–Molecule Reactions. Ion–molecule reactions have been valuable in studies of the structures of long-lived, low-energy radical cations.[35] Many of these studies have been carried out in Fourier-transform ion cyclotron resonance mass spectrometers which allow the isolation of reactant ions and the examination of the progress of the reactions as a function of time. A dual-cell FT-ICR provides the additional advantage that ion–molecule reactions involving the neutral precursor of the ion are avoided. This is very important, especially in studies of radical cations, since these ions are usually highly reactive toward their neutral precursor. A typical experiment[35-37] in a dual-cell FT-ICR involves generation of the ions for example by electron impact in one cell, transfer of the ions into the other cell, collisional cooling, isolation of the desired ion, and reaction with a neutral reagent for a variable period of time. This procedure allows one to study low-energy ions.[38] These ions do not undergo endothermic reactions.

The radical cation of hydroxyacetone (with the same connectivity as its neutral precursor) is expected to react by charge exchange with neutral reagents with ionization energies lower than that[24] of hydroxyacetone (10.0 eV). Indeed, ionizedhydroxyacetone was found to undergo charge exchange with some of the neutral reagents studied. However, electron transfer does not dominate the product distribution for several neutral reagents with low ionization energies (e.g., for cyclopentanone, $\Delta H = -16$ kcal/mol for charge transfer, but this reaction corresponds to only 10% of the product ion distribution). This finding suggests that the radical cation may have partially isomerized to another structure prior to reaction (or exists in an equilibrium with other structures). Further support for the existence of another structure is obtained from the observation of a reaction which is not only

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[35] See, for example: Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649.

[36] Stirk, K. M.; Orlowski, J. C.; Leeck, D. T.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 8604.

[37] Kenttämaa, H. I.; Kiminkinen, L. K. M.; Orlowski, J. C.; Stirk, K. M. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 734.

[38] Lin, P.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1992**, *27*, 1155.

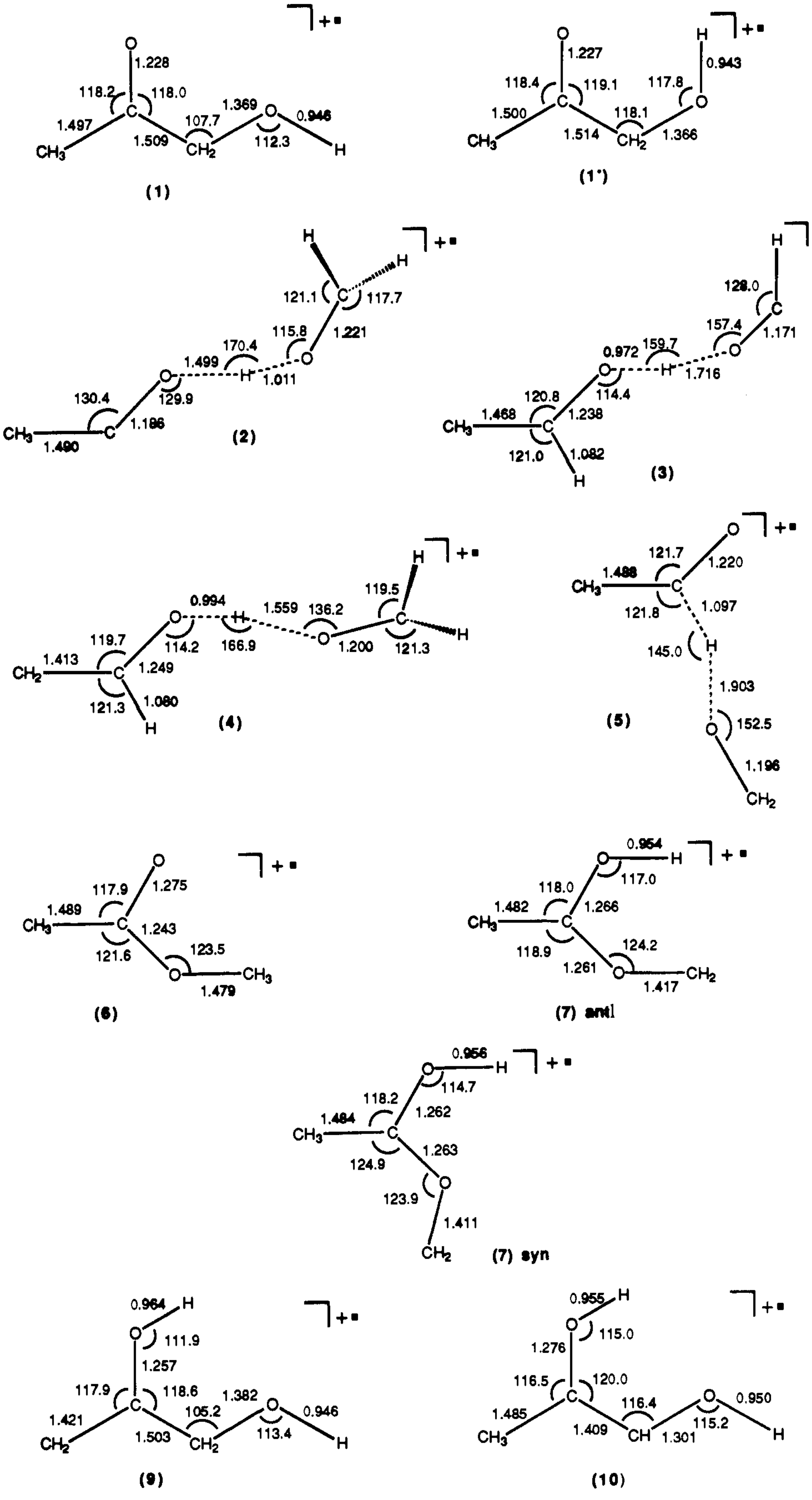

Figure 2. Optimized geometries (6-31G**) of different $[C_3H_6O_2]^{\cdot+}$ structures.

unexpected for the conventional hydroxyacetone radical cation but is unprecedented for any organic radical cation.

The most interesting reaction of ionized hydroxyacetone is the replacement of $CH_3CO^{\bullet}$ in the ion with neutral ketones, aldehydes, and alcohols (Table I). The relatively high rate of this reaction, together with the fact that the reaction is common, provides strong support for a hydrogen-bridged structure for the reactant ion and, specifically, the structure $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**). Similar reactions have not been reported for covalently bonded organic radical cations. Further, replacement of $CH_3CO^{\bullet}$ does not occur for isomeric, covalently bonded ions. For example, exclusive proton transfer takes place[19] upon reaction of the

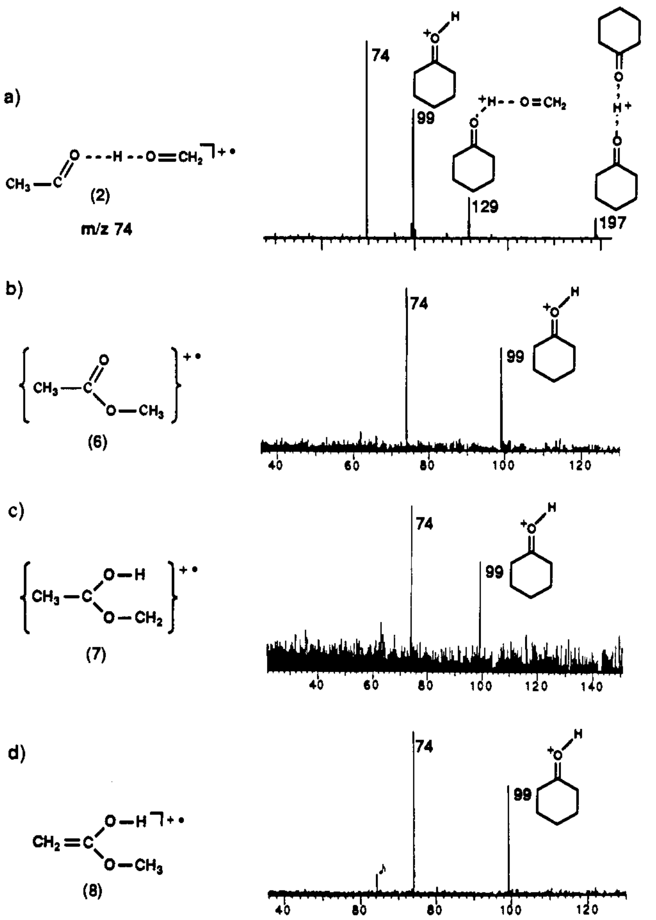

Figure 3. Reaction of (a) ionized hydroxyacetone, (b) ionized methyl acetate (known to have the enol structure), (c) a distonic reference ion (known to have the enol structure), and (d) the enol reference ion with cyclohexanone for 500 ms. The nominal cyclohexanone pressure was 6.0 × 10^{-8} Torr. The musical note in spectrum d denotes interference from a local radio station.

isomeric, ionized methyl acetate (known to have the structure $[CH_2{=}C(OH)OCH_3]^{\bullet+}$) with cyclohexanone (Figure 3b). In fact, charge exchange and proton transfer are *the only reactions* reported[19] for a variety of oxygen-containing radical cations upon reaction with cyclohexanone. However, ionized hydroxyacetone reacts with cyclohexanone by replacement of $CH_3CO^\bullet$ as well as by deprotonation.

In order to examine the $CH_3CO^\bullet$ replacement reaction in more detail, a multiple-stage MS/MS/MS experiment was carried out for propanal as the neutral reagent. The molecular ion of hydroxyacetone was generated in one side of the dual-cell reaction chamber (Figure 4a), transferred into the other cell, isolated (Figure 4b), and allowed to react with propanal. An ion of *m/z* 89, presumably $[CH_3CH_2CHO{\cdots}H{\cdots}O{=}CH_2]^+$, is generated in this reaction (Figure 4c). When this product ion was isolated (Figure 4d) and allowed to react with neutral propanal, it rapidly yielded an ion which corresponds to replacement of CH_2O: $[CH_3CH_2CHO{\cdots}H{\cdots}OCHCH_2CH_3]^+$ (*m/z* 117; Figure 4e). An analogous secondary product ion corresponding to replacement of CH_2O is generated in *all the reactions* wherein replacement of the acetyl radical occurs. This observation provides strong support for the proposed hydrogen-bridged structure of the primary product ion: $[CH_3CH_2CHO{\cdots}H{\cdots}O{=}CH_2]^+$ in the case of propanal. As a summary, the reaction sequence with propanal is initiated by replacement of the less basic part, $CH_3CO^\bullet$, of the hydrogen-bridged ion $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**) with propanal (CH_3CO, PA(O) = 153 kcal/mol;[25] CH_3CH_2CHO, PA = 190 kcal/mol[25]). This reaction is followed by replacement of the less basic part, CH_2O, of the primary product ion $[CH_3CH_2CHO{\cdots}H{\cdots}O{=}CH_2]^+$ (CH_2O, PA = 172 kcal/mol) with another propanal molecule. Finally, it should be noted here that an abundant protonated reagent molecule is also formed upon reactions of the most basic neutral reagents (Table I). For these reagents, the $CH_3CO^\bullet$ replacement in ionized hydroxyacetone is highly exothermic. The reaction is likely to yield a hot product ion which consequently "boils off" a formaldehyde molecule, yielding the protonated reagent molecule.

The reactivity observed for the molecular ion of hydroxyacetone conclusively rules out the structure $[CH_2{=}C(H)O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**4**) for this ion. A hydrogen-bridged ion with structure **4** would react with nucleophiles by replacement of CH_2O ($CH_2{=}CHO$, PA(O) = 185 kcal/mol,[34] CH_2O, PA = 172 kcal/mol[25]). Replacement of CH_2O, however, was not observed.

A minor reaction corresponding to the replacement of $CHO^\bullet$ occurs with reagents with low proton affinities, i.e., dimethyl disulfide and alkyl iodides (Figure 5, Table I). Replacement of $CHO^\bullet$ suggests that some of the hydroxyacetone radical cations, probably the hydrogen-bridged radical cation **2**, isomerizes to $[CH_3C(H){=}O{\cdots}H{\cdots}O{=}CH]^{\bullet+}$ (**3**) under certain conditions (Scheme III). The isomerization/$CHO^\bullet$-replacement reaction is apparently accessible only when replacement of $CH_3CO^\bullet$ is energetically unfavorable, as demonstrated by the finding that the latter reaction does not occur for the weak nucleophiles which show $CHO^\bullet$ replacement. Considering our computational result that the ion **3** is thermodynamically more stable than ion **2** (Table II; see the following discussion on the molecular orbital calculations) and an estimate that the $CHO^\bullet$ replacement in **3** is likely to be as exothermic as the $CH_3CO^\bullet$ replacement in **2** (i.e., both reactions should be observed if both **2** and **3** are present), it is concluded that a relatively high barrier must separate the initially formed ions **2** from the ions **3**. This is not unexpected as hydrogen atom abstraction by a radical often has a substantial activation energy associated with it.[39] Apparently, isomerization occurs to a small proportion of the ions **2** within an ion–molecule collision complex if other faster channels are not accessible (e.g., replacement of $CH_3CO^\bullet$).

For some of the reactions studied, a plot of the relative abundance of the hydroxyacetone radical cation as a function of reaction time was curved, i.e., part of the radical cations appeared unreactive. This finding provides further support for the existence of at least two ion structures among the hydroxyacetone ions. Consideration of the types of reactions observed for each neutral reagent and the reactions expected for the covalently bonded and hydrogen-bridged ions **1** and **2** leads to the conclusion that the unreactive reactant ions observed in some of the experiments have the conventional, covalently bonded structure. For example, cyclohexanone is expected to react with the covalently bonded ion **1** by charge exchange and with the ion **2** by $CH_3CO^\bullet$ replacement. Hence, both isomeric forms, if present, should react with cyclohexanone. In agreement with this expectation, a complete reaction takes place for cyclohexanone. However, propanal has a significantly higher ionization energy (IE = 10.0 eV) than cyclohexanone and will not react by electron transfer with the covalently bonded ions. Indeed, some of the hydroxyacetone radical cations were found to be unreactive toward propanal.

The proportion of unreactive ions observed for propanal increased substantially (from 5% to about 30%) when ionization of hydroxyacetone was carried out using thermoneutral charge exchange instead of electron ionization (a similar observation was made for several other reagents). Hence, generation of the molecular ion with only a small amount of internal energy (charge exchange) results in a larger amount of unreactive ions, a finding that supports the proposal made above that the unreactive ions have the original covalently bonded structure **1**.

Even when generated by charge exchange, part of the ions **1** have enough internal energy to overcome the isomerization barrier

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[39] Pross, A.; Yamataka, H.; Nagase, S. *J. Phys. Org. Chem.* **1991**, *4*, 135.

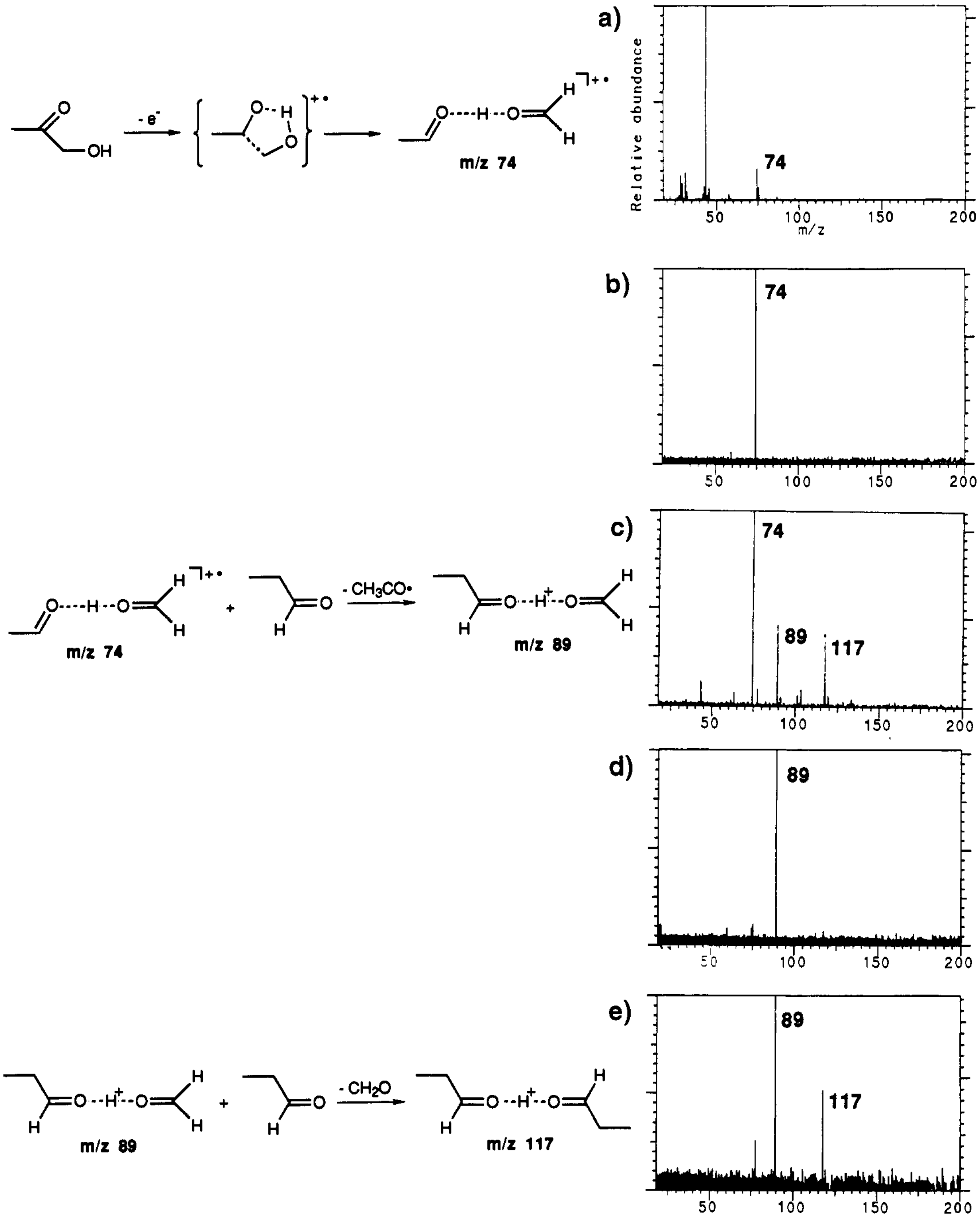

Figure 4. A typical MS/MS/MS experiment. (a) Electron ionization of hydroxyacetone, (b) isolation of the molecular ion of *m/z* 74 transferred into the other side of the dual-cell reaction chamber, (c) reaction of ionized hydroxyacetone with propanal for 500 ms, (d) isolation of the product ion *m/z* 89, and (e) reaction of this ion with propanal for 250 ms.

to **2**. The isomerization must occur *prior to* formation of a collision complex with a neutral reagent molecule because the amount of internal energy gained by the ions upon ionization (but lost during collisional cooling prior to reaction studies) was observed to have a strong effect on the reaction products. Further, the results suggest that the two structures **1** and **2** do not exist in a dynamic equilibrium in the experiments discussed here. Indeed, such an equilibrium is prevented by the use of collisional cooling to remove the excess internal energy of the ions after generation and prior to examination of their chemical reactions.

Ab Initio Molecular Orbital Calculations

Eleven isomeric $[C_3H_6O_2]^{\bullet+}$ structures, including two different conformations of the covalently bonded hydroxyacetone radical cation, two ionized enols, ionized methyl acetate, two distonic methyl acetate ions and four hydrogen-bridged radical cations, were examined computationally (Table II). The geometries were optimized in a stepwise manner up to the 6-31G** level of theory (Figure 2). The final relative energies were determined using a single-point calculation at the MP2/6-31G**//6-31G**+ZPVE level of theory. Electron correlation at the MP2 level was found to have a significant effect in the relative energies (Table II). The spin contamination, $\langle S^2 \rangle$, for the single-point calculations reported is within acceptable range (from 0.759 to 0.774) and close to the value of 0.75 for the pure spin state.

The calculations show that the covalently bonded ionized hydroxyacetone (**1**) corresponds to an energy minimum. The greatest positive charge in this ion is on the carbonyl carbon (0.49) and the greatest atomic spin density on the carbonyl oxygen (1.06). In the lowest-energy conformer (**1**), the hydroxylic hydrogen is pointing away from the carbonyl oxygen (C–CH₂–O–H dihedral angle 183.3°). The conformer wherein the

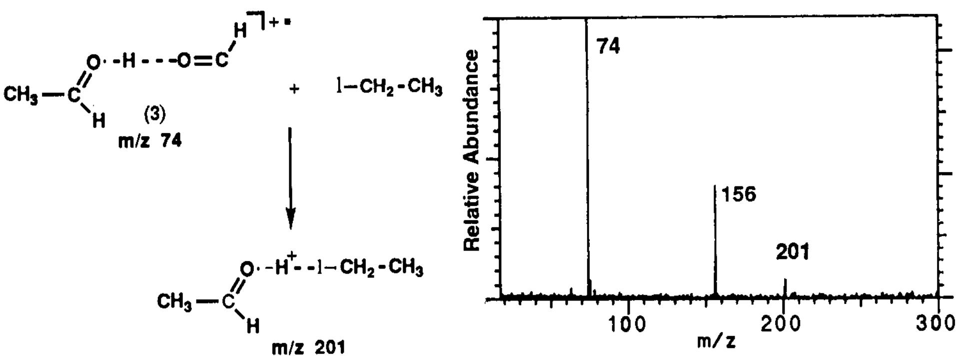

Figure 5. Reaction of ionized hydroxyacetone with ethyl iodide for 250 ms, resulting in ionized ethyl iodide (*m/z* 156) and a product ion of *m/z* 201 arising from replacement of $CHO^{\bullet}$ in the ion.

hydroxylic hydrogen is pointing toward the carbonyl oxygen (C–CH_2–O–H dihedral angle 0.0°) (1′), a structure of interest since it is likely to lead to rearrangement to the hydrogen-bridged radical cation $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**), was found to be a transition state and 7.3 kcal/mol higher in energy than the other conformer studied.

The hydrogen-bridged radical cation $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**) is calculated to be more stable (by 10.2 kcal/mol) than the covalently bonded ionized hydroxyacetone at the MP2/6-31G**//6-31G**+ZPVE level of theory. The other experimentally observed hydrogen-bridged radical cation, $[CH_3C(H)O{\cdots}H{\cdots}O{=}CH]^{\bullet+}$ (**3**), was found to be more stable by 3.3 kcal/mol than structure **2** and more stable by 13.5 kcal/mol than ionized hydroxyacetone. The greatest difference between the two hydrogen-bridged structures is in the lengths of the -O···H···O- bonds. In structure **2**, the CH_2O—H bond is shorter (1.011 Å) than the hydrogen bond to the acyl radical (1.499 Å). This finding agrees with the relative proton affinities of the hydrogen-bonded molecules (CH_3CO, PA(O) = 153 kcal/mol; CH_2O, PA = 172 kcal/mol),[25] as well as with the observation that the acetyl radical is readily replaced in the ion by neutral molecules, as discussed above. In the other hydrogen-bridged structure, the ion $[CH_3C(H){=}O{\cdots}H{\cdots}O{=}CH]^{\bullet+}$ (**3**), the bond length to acetaldehyde is shorter (0.972 Å) than to the formyl radical (1.716 Å). This result is in agreement with the relative proton affinities of the hydrogen-bonded molecules (CH_3CHO, PA = 187 kcal/mol; CHO, PA(O) = 146 kcal/mol),[25] as well as with the proposal that the replacement of the formyl radical by neutral molecules involves this hydrogen-bridged structure. The greatest positive atomic charges in both hydrogen-bridged structures were found, expectedly, at the bridged hydrogens (0.52 for **2** and 0.47 for **3**). The greatest atomic spin densities are located at the acyl carbonyl carbon in structure **2** (0.84) and at the formyl carbon in structure **3** (0.80).

The hydrogen-bridged radical cation $[CH_2{=}C(H)O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**4**) was studied computationally because of the earlier suggestion[15,20,23] that the internally excited and short-lived ionized hydroxyacetone may isomerize to this hydrogen-bridged species via the intermediacy of the ion **2** (see Scheme II). Indeed, the hydrogen-bridged radical cation $[CH_2{=}C(H)O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**4**) was found to be the most stable out of the four hydrogen-bridged structures studied. The final relative energy of this structure was calculated to be 17.5 kcal/mol lower than that of ionized hydroxyacetone. Positive charge is again localized to the bridging hydrogen (0.49), and the greatest atomic spin density is at the vinyl CH_2 carbon (0.94). The hydrogen bond length to the vinyl portion is shorter (0.994 Å) than to formaldehyde (1.559 Å). Hence, this ion would be expected to react with neutral molecules by replacement of formaldehyde, a reaction which was not observed for any of the neutral reagents studied. It is concluded that in spite of the great stability of this ion, it is not generated from the long-lived, low-energy radical cation of hydroxyacetone.

The -C···H···O- hydrogen-bridged radical cation $[CH_3C(O){\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**5**) was of interest because of a recent proposal that this ion, and not $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**), is the key intermediate in the fragmentation of ionized methyl acetate to CH_3CO^+ and $^{\bullet}CH_2OH$.[23] The ion **5** was calculated to be the least stable out of the four hydrogen-bridged radical cations studied. The hydrogen bond length to formaldehyde is unusually long (1.903 Å; that to the acetyl portion is only 1.097 Å). The charge density is smaller at the bridging hydrogen (0.33) than in the other hydrogen-bridged structures studied, and the greatest atomic spin density is localized to the carbonyl oxygen (1.04). Hence, this ion corresponds to an ion-neutral complex in which the radical cation of acetaldehyde and a neutral formaldehyde are held in association chiefly by electrostatic attractions. An ion with this structure is expected to decompose to $CH_3CHO^{\bullet+}$ and CH_2O upon activation and to react with neutral molecules by replacement of formaldehyde. Neither type of reactivity was observed in this study. It is concluded that this structure is highly unlikely for the long-lived, low-energy radical cation of hydroxyacetone.

A few additional covalently bonded ions were also studied computationally. These include ionized methyl acetate (**6**), which is calculated to be 8.3 kcal/mol more stable than ionized hydroxyacetone (**1**) and 1.9 kcal/mol less stable than the hydrogen-bridged radical cation **2**. Further, two conformations of the distonic methyl acetate **7**, the syn and anti conformations in view of the C–C–O–C skeleton, were examined. The syn conformer was found to be 14.4 kcal/mol and the anti conformer 12.5 kcal/mol more stable than ionized methyl acetate. Finally, the two enol isomers of ionized hydroxyacetone were found to be by far the most stable structures studied. 2,3-Dihydroxy-1-propenyl radical cation, $[CH_2{=}C(OH)CH_2OH]^{\bullet+}$ (**9**), is 22.3 kcal/mol and 1,2-dihydroxy-1-propenyl radical cation, $[CH_3C(OH){=}CHOH]^{\bullet+}$ (**10**), is 41.2 kcal/mol more stable than ionized hydroxyacetone. In these ions, the greatest positive atomic charge (0.50 and 0.46 for **9** and **10**, respectively) is located at the middle sp^2-carbon atom and the greatest atomic spin density (0.96 and 0.62, respectively) at the terminal sp^2-carbon. In spite of the low relative energies of these ions, there is no experimental evidence for their generation from the radical cation of hydroxyacetone. This is probably explained by high energy barriers associated with the 1,3- and 1,4-hydrogen shifts needed for the isomerization of ionized hydroxyacetone to these structures.

Conclusions

A significant proportion of the long-lived, low-energy radical cations of hydroxyacetone have a hydrogen-bridged structure, most likely $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**). The strongest evidence in support of the existence of this structure is obtained from the examination of the reactivity of ionized hydroxyacetone: neutral carbonyl compounds and alcohols rapidly replace the acetyl radical in the ion. This reactivity is unique for a radical cation. The extent of isomerization of the covalently bonded

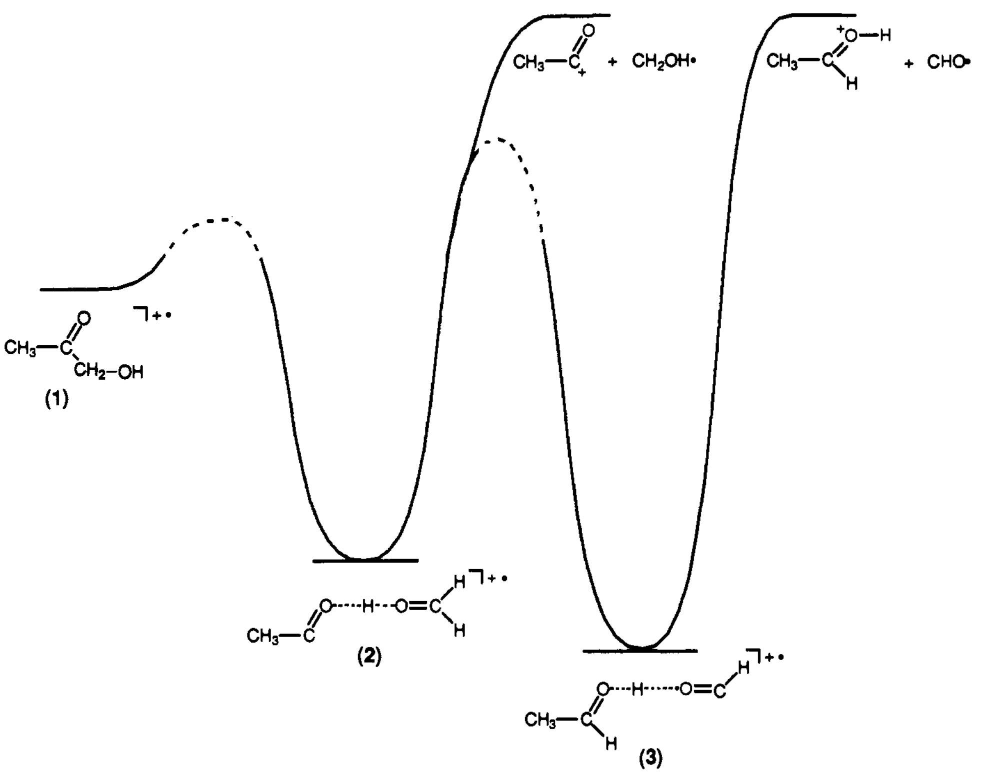

Figure 6. Potential energy diagram showing the calculated relative energies of the covalently bonded, ionized hydroxyacetone and two hydrogen-bridged isomers (ions **2** and **3**), as well as the threshold energies for two dissociation reactions.

hydroxyacetone radical cation to the hydrogen-bridged ion **2** can be reduced by generating the radical cation with only small amounts of internal energy (using thermoneutral electron transfer). This finding suggests that the isomerization occurs prior to formation of a collision complex with a neutral reagent.

Further isomerization of the ion **2** to yield another hydrogen-bridged radical cation, $[CH_3C(H){=}O{\cdots}H{\cdots}O{=}CH]^{\bullet+}$ (**3**), apparently takes place under certain conditions (Scheme III). This isomerization occurs upon collision-activated dissociation of the molecular ion, eventually leading to loss of $CHO^{\bullet}$, as well as for the low-energy ions, as demonstrated by replacement of $CHO^{\bullet}$ in some of the long-lived, low-energy radical cations upon reaction with certain neutral molecules. This rearrangement may occur within a collision complex with a neutral reagent but apparently only if more favorable reactions are not accessible. The replacement of $CHO^{\bullet}$ always corresponds to a minor pathway and is not observed for most of the neutral reagents studied, in spite of the prediction obtained by *ab initio* molecular orbital calculations that the structure **3** is more stable than **1** and **2**. It is concluded that there must be a substantial barrier on the reaction coordinate for the hydrogen atom transfer in **2** leading to structure **3** (Figure 6).

Ab initio molecular orbital calculations indicate that there are several stable hydrogen-bridged structures on the $[C_3H_6O_2]^{\bullet+}$ potential energy surface. The experimentally observed structure $[CH_3C{=}O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**2**) corresponds to a potential energy minimum, being more stable by 10.2 kcal/mol than ionized hydroxyacetone at the MP2/6-31G**//6-31G**+ZPVE level of theory. However, **2** does not correspond to the global minimum on this surface: the enol isomers of ionized hydroxyacetone are the most stable of all the structures studied (22.3 and 41.2 kcal/mol more stable than ionized hydroxyacetone). There is no experimental evidence for the generation of these structures, however. This is probably explained by high energy barriers associated with isomerization through 1,3- and 1,4-hydrogen shifts.

This study shows that the long-lived, low-energy radical cations of hydroxyacetone behave somewhat differently from the internally excited, short-lived radical cations investigated before.[15,20,23] The internally excited ions have been suggested to isomerize[15,20,23] via the ion **2** to the hydrogen-bridged ion $[CH_2{=}C(H)O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**4**), which then rearranges to **3** prior to or during dissociation. If this isomerization sequence occurred for the long-lived ions, ion **4** would be expected to be the dominant structure since it is calculated to be more stable than the other structures involved (**1**–**3**). However, the experimental evidence presented here shows that the ion $[CH_2{=}C(H)O{\cdots}H{\cdots}O{=}CH_2]^{\bullet+}$ (**4**) is not generated from the long-lived, low-energy radical cation of hydroxyacetone. This finding suggests the presence of a high barrier on the isomerization pathway leading to ion **4**.

Acknowledgment. The Academy of Finland, Joensuu University, and the Finnish Chemical Society, together with the National Science Foundation (CHE-9107121) and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, are thanked for financial support of this work.