J. Am. Chem. Soc. **1994**, *116*, 7807–7814

Hydrogen-Bridged Ions $[CH_3C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}$, $[CH_2{=}C(H)O\cdots H\cdots O{=}CH_2]^{\bullet+}$, and $[CH_3C(H)O\cdots H\cdots O{=}CH]^{\bullet+}$ and Ion–Dipole Complex $[CH_3C(=O)^+\cdots O(H)CH_2^\bullet]$: Their Role in the Dissociation Chemistry of Ionized Acetol, $CH_3C(=O)CH_2OH^{\bullet+}$

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Received December 20, 1993. Revised Manuscript Received April 20, 1994[⊗]

Abstract: The remarkable unimolecular chemistry of the acetol cation radical, $CH_3C(=O)CH_2OH^{\bullet+}$ (**4**), has been studied by a wide range of mass spectrometric experiments. A detailed analysis of the D-labeled isotopomers of **4**, $CH_3C(=O)CD_2OH^{\bullet+}$ and $CH_3C(=O)CH_2OD^{\bullet+}$, shows that the hydrogen-bridged ion $[CH_3C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**3a**), a key intermediate on the (related) methyl acetate (**1**) hypersurface, does not participate in the low-energy rearrangement reaction: $\mathbf{4} \rightarrow CH_3CHOH^+ + HC{=}O^\bullet$. Integration of the experimental information with the results of *ab initio* molecular orbital calculations (executed at the UMP3/6-31G*//4-31G+ZPVE level of theory and for the key ions **4**, **3a**, and **3b** also at the UMP3/6-31G**//6-31G** and UMP3/6-31G*//UMP2/6-31G* levels) provides evidence that the loss of $HC{=}O^\bullet$ from **4** involves isomerization into the ion–dipole complexes $CH_3C(=O)^+\cdots O(H)CH_2^\bullet$ (**4a**) and $CH_3C(=O)H^{\bullet+}\cdots O{=}CH_2$ (**3b**). It is further proposed that the hypersurfaces of ionized acetol and methyl acetate have no common features. The calculations also predict that another stable O···H···O hydrogen-bridged isomer, $[CH_2{=}C(H)O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**6**) does not communicate with **4** or **3a**. This isomer was independently generated and characterized: at elevated energies it behaves as a vinyl alcohol ion–formaldehyde complex, and the experiments confirm that it does not communicate with either the acetol or the methyl acetate hypersurface.

Introduction

Structural isomerization in gas-phase ions has received steadily increasing attention during the past 15 years. By using the combined information from mass spectrometric techniques and *ab initio* molecular orbital theory calculations,[1] the gas-phase chemistry of a number of stable ions of unexpected structure has been unraveled. These include ylide, distonic, and hydrogen-bridged radical cations such as $CH_2OH_2^{\bullet+}$, $CH_2CH_2OH_2^{\bullet+}$, and $[CH_2{=}CHO\cdots H\cdots OH_2]^{\bullet+}$, respectively. The latter ions appear to be remarkably stable, but in contrast to their more familiar even-electron counterparts (e.g., proton-bound dimers[1d] such as $[CH_3CH{=}O\cdots H\cdots OH_2]^+$), their generation and identification are less straightforward.[1b] One system that has been carefully explored by experiment and by theory involves the potential energy surface for the isomeric $C_3H_6O_2^{\bullet+}$ ions related to ionized methyl acetate.[1a,b] Interest in this system was sparked by the observation that a majority of low-energy molecular ions of methyl acetate lost $^\bullet CH_2OH$ rather than $CH_3O^\bullet$ in the formation of the acetyl cation, CH_3CO^+. The key experiment was the collision-induced dissociative ionization of the free-radical products from metastable methyl acetate molecular ions.[2]

Heinrich et al., in an *ab initio* computational study,[3] provided an elegant explanation which involved *inter alia* the reaction sequence:

$$\underset{\mathbf{1}}{CH_3C(=O)OCH_3^{\bullet+}} \rightarrow \underset{\mathbf{2}}{CH_3C^+(OH)OCH_2^\bullet} \rightarrow$$

$$\underset{\mathbf{3a}}{[CH_3C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}} \rightarrow CH_3C{=}O^+ + {}^\bullet CH_2OH$$

It should be noted, however, that the key intermediate **3a**, an O···H···O hydrogen-bridged radical cation,[1,4] although of similar stability to the molecular ion, was found to be generated at an energy which results in its spontaneous dissociation. This is because the isomerization barrier for $\mathbf{2} \rightarrow \mathbf{3a}$ lies above the summed product enthalpies. Thus ion **3a**, derived from ionized methyl acetate, represents a transient species, i.e., is probably experimentally inaccessible via this system because it may survive for no more than a few vibrations. Analysis by Rice–Ransperger–Kassel–Marcus (RRKM) theory[5] of the time dependence of the loss of $^\bullet CH_2OH$ from metastable **1** seems to indicate that indeed only the distonic ion **2** may be involved as an observable intermediate. Nevertheless, there must be at least a transition state that is fairly distinct from **2**, presumably resembling **3a**, in its geometry.

The H-bridged ion **3a** conceivably can be generated from ionized acetol (1-hydroxypropan-2-one) (**4**) *viz.*

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[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1994.

(1) For selected reviews, see: (a) Heinrich, N.; Schwarz, H. In *Ion and Cluster Ion Spectroscopy and Structure*; Maier, J. P., Ed.; Elsevier: Amsterdam, 1989; p 329. (b) Burgers, P. C.; Terlouw, J. K. In *Specialist Periodical Reports*: *Mass Spectrometry*; Rose, M. E., Ed.; The Royal Society of Chemistry: London, 1989; Vol. 10, Chapter 2. (c) Radom, L. *Org. Mass Spectrom.* **1991**, *26*, 359. (d) Uggerud, E. *Mass Spectrom. Rev.* **1992**, *11*, 389.

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$$\underset{\mathbf{4}}{CH_3C(=O)CH_2OH^{\bullet+}} \rightarrow \underset{\mathbf{3a}}{[CH_3C=O\cdots H\cdots O=CH_2]^{\bullet+}}$$

via a mechanism similar to that which is proposed to initiate the loss of HCO$^\bullet$ from ionized ethylene glycol.[6] We considered the above reaction some years ago[2] but could provide no supporting experimental evidence. However, recently, Kenttämaa and coworkers[7a,b] have described an ion–molecule study of the reactivity of ionized acetol **4** using the technique of FT-ICR.[7c] It was proposed that long-lived **4** ions have partially isomerized to **3a** and that some of the latter rearrange to $[CH_3C(H)=O\cdots H\cdots O=CH]^{\bullet+}$ (**5a**), a second $-O\cdots H\cdots O-$ bridged species.

$$\underset{\mathbf{4}}{CH_3C(=O)CH_2OH^{\bullet+}} \rightarrow \underset{\mathbf{3a}}{[CH_3C=O\cdots H\cdots O=CH_2]^{\bullet+}} \rightarrow \underset{\mathbf{5a}}{[CH_3C(H)=O\cdots H\cdots O=CH]^{\bullet+}}$$

We have entertained this reaction sequence involving ion **5a** to rationalize the experimental observation that *metastable* ions **4** predominantly produce CH_3CHOH^+ ions by loss of HCO$^\bullet$ (>95%) in a reaction characterized by a very small kinetic energy release, $T_{0.5}$ = 3 meV,[2] 2.0 meV (this work). However, on the basis of energy measurements described hereunder, this attractive scheme requires that isomerization barriers lie less than 10 kcal mol^{-1} above $\Delta H_f°(\mathbf{4})$. *Ab initio* calculations have shown that the barrier heights involved in the chemistry of O···H···O bridged ions are often considerably higher,[8] and indeed a preliminary *ab initio* calculation for the transition state **4** → **3a** was not encouraging. In this work we describe multiple collision experiments on deuterium-labeled acetol ions, energy measurements, and *ab initio* computational results. It will be shown that the simple sequence $\mathbf{4} \rightarrow \mathbf{3a} \rightarrow \mathbf{5a} \rightarrow CH_3CHOH^+ + HC{=}O^\bullet$ is at odds with the deuterium labeling experiments. Similarly, the independently generated and characterized O···H···O bridged isomer $[CH_2=CHO\cdots H\cdots O=CH_2]^{\bullet+}$ (**6**) is not involved in the dissociation chemistry of **4**. A pathway to CH_3CHOH^+ which satisfies all of our experimental observations and which is supported by *ab initio* calculations involves dissociation via a series of ion–dipole complexes, as will be described below.

Experimental and Theoretical Methods

The metastable ion (MI) spectra were obtained with the Ottawa University VG Analytical ZAB-2f and KRATOS MS 902 mass spectrometers. Appearance energy (AE) values were measured by Dr. F. P. Lossing, using the procedure described in ref 9. Metastable AE measurements were performed as described in ref 10. All collision experiments were performed on the McMaster VG Analytical ZAB-R mass spectrometer of $BE_1(\perp Q)E_2$ geometry as described in ref 11. The collision-induced dissociation (CID) and neutralization–reionization (NR)[12] spectra (8-keV ions) were obtained in the second field-free region (^{2}ffr) using O_2 to effect collision-induced dissociation (CID) or reionization (main beam transmission, 80%) and *N,N*-dimethylaniline vapor for neutralization.[13] The structure of the products of spontaneous or collision-induced dissociations ions in the ^{2}ffr was probed by obtaining their CID mass spectra in the third field-free region (^{3}ffr) using O_2 as the collision gas and mass-selected precursor ions of 10 keV translational energy.[14]

$CH_3C(=O)CD_2OH$ was synthesized by reducing the thioketal of methyl pyruvate[15a] with $LiAlD_4$ and decomposing the product by the method of Corey et al.[15b] The solid, recrystallized HgCl adduct was admitted to the ion source via the solids probe. All other compounds used were commercially available (Aldrich) and purified where necessary. Deuteration of the hydroxyl groups in $CH_3C(=O)CH_2OH$ and $BrCH_2CHOHCH_2OH$ was achieved by dissolving a small amount of sample in CH_3OD, after which methanol was removed; this was repeated three times.

Standard *ab initio* MO calculations were performed with both the Gaussian 90 (G90)[16] and 92 (G92)[17] systems of programs, using the unrestricted Hartree–Fock (UHF) procedure. Optimized geometries, harmonic frequencies, and zero-point vibrational energies (ZPVEs)[18] were obtained using the standard 4-31G[19] split-level basis set. Single-point energies on the 4-31G geometries were obtained using the 6-31G*[19,20] basis set, and correlation was included employing the Møller–Plesset perturbation theory terminated at the third order[21] (UMP3/6-31G*//4-31G).

G92 was also used for a limited set of calculations (involving the key ions **4**, **3a**, and **3b**) in which UMP2/6-31G* (FC) geometry optimizations were performed, followed by single-point UMP3/6-31G* calculations. In addition, UMP3/6-31G**//UHF/6-31G** results are presented for ions **4**, **3a**, **3b**, and **5a**, for which MP2/6-31G**//UHF/6-31G** results have very recently been reported in ref 7b. In the latter study, the optimized acetol$^{\bullet+}$ geometry chosen as the reference point for the calculation of the relative energies clearly is not the conformer of lowest energy, and this may explain an apparent discrepancy with the results presented in Table 1 of this study.

Frequency calculations gave the correct number of negative eigenvalues for all minima and transition states (TS) reported in Figure 1 (optimized geometries) and Table 1 (energies). For all species investigated the spin contamination was acceptable, within 10% of 0.75, or, for even-electron species, $\langle s^2\rangle = 0.0$. All UHF wave functions were checked for internal instabilities.

Results and Discussion

Ionized acetol has two dissociation reactions of low energy requirement, as shown in Scheme 1. Both reactions take place

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Table 1. Total Energies (Hartrees), Zero-Point Vibrational Energies (ZPVE), and Relative Calculated Energies (E_{rel}, kcal/mol[a]) for Some Isomers and Components of the (Acetol)$^{\bullet+}$ System

structure	state	UHF/4-31G	UHF/6-31G*//4-31 G	UMP3/6-31G*//4-31 G	ZPVE	E_{rel}
$CH_3C{=}O\cdots H\cdots O{=}CH_2^{\bullet+}$ (**3a**)	$^2A'$	–266.102 92	–266.493 15	–267.216 75	51.0	–2.1
$CH_3C({=}O)\cdots H\cdots O{=}CH_2^{\bullet+}$ (**3b**)	$^2A'$	–266.093 39	–266.486 54	–267.197 70	50.3	9.2
$CH_3C({=}O)CH_2OH^{\bullet+}$ (**4**)	$^2A'$	–266.108 93	–266.499 33	–267.216 51	52.9	0
$CH_3C({=}O)^+\cdots O(H)CH_2^\bullet$(**4a**)	^2A	–266.097 67	–266.489 32	–267.215 46	50.8	–1.4
(**4b**)	^2A	–266.096 25	–266.480 86	–267.211 78	51.3	1.7
$CH_3C(H){-}O\cdots H\cdots O{=}CH^{\bullet+}$ (**5a**)	$^2A'$	–266.107 14	–266.500 44	–267.224 38	50.8	–7.0
$CH_3C(OH)\cdots H\cdots O{=}CH^{\bullet+}$ (**5b**)	$^2A'$	–266.090 15	–266.487 67	–267.210 63	50.5	1.3
$CH_2{=}CHO\cdots H\cdots O{=}CH_2^{\bullet+}$ (**6**)	$^2A''$	–266.120 04	–266.508 55	–267.230 63	51.6	–10.0
$CH_3C^+(OH)CH_2O^\bullet$(**7**)	^2A	–266.101 85	–266.489 68	–267.203 30	53.7	9.1
(**7a**)	$^2A'$	–266.116 80	–266.502 43	–267.216 33	52.9	0.5
$CH_3CH(OH)C(H){=}O^{\bullet+}$ (**8**)	^2A	–266.086 02	–266.478 58	–267.196 66	53.0	12.5
$CH_2{=}C(OH)CH_2OH^{\bullet+}$ (**9**)	$^2A''$	–266.132 15	–266.517 86	–267.246 22	54.1	–17.0
TS **4**–**7**	^2A	–266.074 32	–266.467 37	–267.196 78	50.7	10.2
TS **4a**→**4b**	^2A	–266.096 23	–266.481 27	–267.211 52	51.1	1.3
TS **4a**→**3b**	$^2A'$	–266.070 50	–266.467 76	–267.203 31	48.3	3.7
TS **3b**→**5a**	$^2A'$	–266.073 36	–266.466 12	–267.195 34	47.5	7.9
TS **6**–**5a**	^2A	–266.037 54	–266.438 93	–267.183 28	48.9	16.8
TS **6**–**3a**	^2A	–266.011 63	–266.409 49	–267.139 96	48.2	43.3
TS **7**–**8**	^2A	–266.048 75	–266.449 46	–267.172 04	51.2	26.3

structure	state	UHF/6-31G**	UMP3/6-31G**//UHF/6-31G**	ZPVE	E_{rel}
$CH_3C{=}O\cdots H\cdots O{=}CH_2^{\bullet+}$ (**3a**)	$^2A'$	–266.514 13	–267.272 41	51.5	–2.6
$CH_3C({=}O)\cdots H\cdots O{=}CH_2^{\bullet+}$ (**3b**)	$^2A'$	–266.499 90	–267.247 14	50.0	11.8
$CH_3C({=}O)CH_2OH^{\bullet+}$ (**4**)	$^2A'$	–266.517 27	–267.270 55	52.8	0
$CH_3C(H){-}O\cdots H\cdots O{=}CH^{\bullet+}$ (**5a**)	$^2A'$	–266.520 56	–267.278 44	50.9	–6.9

structure	state	UMP2/6-31G*	UMP3/6-31G*//UMP2/6-31G*	ZPVE	E_{rel}
$CH_3C{=}O\cdots H\cdots O{=}CH_2^{\bullet+}$ (**3a**)	^2A	–267.201 05	–267.221 00	52.0	3.1
$CH_3C({=}O)\cdots H\cdots O{=}CH_2^{\bullet+}$ (**3b**)	^2A	–267.194 11	–267.211 51	52.5	9.6
$CH_3C({=}O)CH_2OH^{\bullet+}$ (**4**)	^2A	–267.212 26	–267.230 24	54.7	0

[a] The relative calculated energies include scaled zero-point vibrational contributions, 0.9 for UHF and 0.96 for UMP2.

close to their thermochemical thresholds.[22] Reaction 1 may represent a simple bond cleavage, and, not surprisingly, this process dominates the normal mass spectrum. The collision-induced dissociation (CID) mass spectrum of the stable (long-lived, i.e., lifetimes > 10^{-5} s) mass-selected acetol ions was also dominated by this process (minor peaks at *m/z* 29, 31, and 42 were also present, 4, 7, and 6% of *m/z* 43, respectively), thus showing that these ions have either retained their structure or rearranged into species from which the same fragments readily can be generated, e.g., the hydrogen-bridged ion $[CH_3C{=}O\cdots H\cdots O{=}CH_2]^{\bullet+}$ (**3a**). The neutralization–reionization (NR) mass spectrum of long-lived acetol ions, see Figure 2a, is again dominated by *m/z* 43, in keeping with the above.[24] The recovered molecular ion is very weak, only ca. 1% of the base peak, *m/z* 43. Note that the energy requirement for methyl acetate ions to yield $CH_3CO^+ + {}^\bullet CH_2OH$ is closely similar to that for acetol ions (14 vs 13 kcal/mol, respectively), but the former exhibits a much more intense recovery ion (8%) relative to the same base peak, *m/z* 43. The much lower acetol ion recovery signal can be reconciled with facile rearrangement into an ion such as **3a** (see above), which upon neutralization should wholly dissociate to $CH_3CO^\bullet + {}^\bullet CH_2OH$ and/or a significant distortion of the molecule, postionization.

Thus, whereas the CID and NR mass spectra provide no clear evidence for the presence of rearranged species, the metastable ion (MI) mass spectrum is dominated by reaction 2, (see Introduction), a process requiring rearrangement of the acetol ion. Reaction 1 contributes the remaining 5% of the MI mass spectrum.[25] The effect on the MI mass spectrum of slowly admitting collision gas is to cause a major increase in *m/z* 43, while *m/z* 45 is essentially unaffected, showing that the ion which leads to the $C_2H_5O^+$ product is present only in very low abundance among stable acetol ions. The MI and CID mass spectra of ionized CH_3COCH_2OD displayed no unexpected features: *m/z* 43 remained base peak in the normal and CID mass spectra, and *m/z* 45 in the MI mass spectrum was cleanly shifted to *m/z* 46 and *m/z* 31 to *m/z* 32. The absence of H/D mixing prior to the principal dissociation to $[CH_3CO]^+$ rules out involvement with any long-lived ion structures associated with the ionized methyl acetate hypersurface, where H/D loss of positional identity approaches the statistical limit among metastable ions.[1a]

In the recent FT-ICR study,[7a] the reactivity of stable acetol ions was explained by the introduction of ions **3a** and **5a**. As shown in Table 1, which summarizes *ab initio* calculations performed in the present work, both ions are stable species, having $\Delta H_f°$ values well below the acetol ion's dissociation limit. Note that the calculated relative energies agree well with estimates based on the empirical relationship[26] for the stabilization energy of O···H···O proton-bound dimers. In the absence of further evidence, our experimental results can be rationalized by the

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(22) The appearance energies (AE) for *m/z* 43 and *m/z* 45 were measured using energy-selected electrons[9] to be 10.35 ± 0.05 and 10.25 ± 0.05 eV; the same value within experimental error was obtained for the AE of the weak metastable peak[10] at *m/z* 43, and that for *m/z* 45 was measured as 10.30 ± 0.1 eV. These results are in keeping with the fragment ions $[CH_3CO]^+$ and $[CH_3CHOH]^+$ being generated at their thermochemical thresholds ($\Delta H_f°$($[CH_3COCH_2OH]$) = –86.5 kcal/mol (by additivity[23a]), $\Delta H_f°$($[CH_3CO]^+$) = 156 kcal/mol,[23b] $\Delta H_f°$($[CH_3CHOH^+]$) = 139 kcal/mol,[23b] $\Delta H_f°$($[HCO^\bullet]$) = 10.7 kcal/mol,[23b] and $\Delta H_f°$($[CH_2OH^\bullet]$) = –4.5 kcal/mol[23b], namely 10.32 and 10.25 eV, respectively. The ionization energy (IE) of acetol was measured using energy-selected electrons as 9.74 ± 0.05 eV, leading to $\Delta H_f°$($[CH_3COCH_2OH]^{\bullet+}$) = 138 kcal/mol.

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(24) The larger part of the *m/z* 29 peak in this spectrum results from the collision-induced dissociative ionization (CIDI) mass spectrum of the neutral species generated from the metastable acetol ions (see Experimental Section). The CIDI spectrum showed only four significant peaks at *m/z* 31 (16%), *m/z* 30 (3%), *m/z* 29 (100%), and *m/z* 28 (23%), an observation entirely in keeping with the formation of $HCO^\bullet$ and ${}^\bullet CH_2OH$ radicals.

(25) The shape of the latter metastable peaks ($T_{0.5}$ = 15 meV) is not Gaussian, having a broader residual collision-induced base beneath a narrow component, also associated with a very small $T_{0.5} \leq 0.5$ meV.

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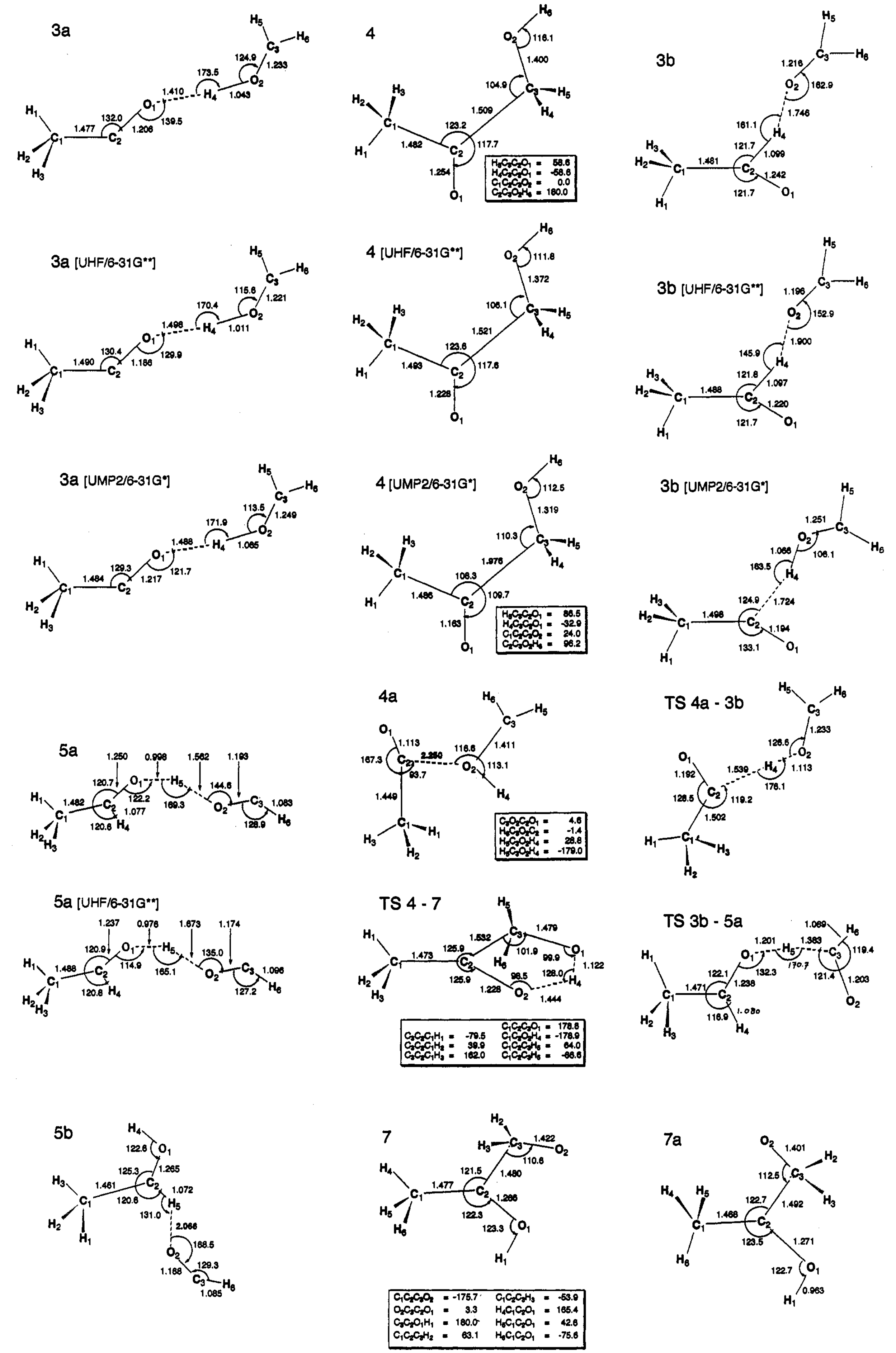

3a
4
3b
3a [UHF/6-31G**]
4 [UHF/6-31G**]
3b [UHF/6-31G**]
3a [UMP2/6-31G*]
4 [UMP2/6-31G*]
3b [UMP2/6-31G*]
5a
4a
TS 4a - 3b
5a [UHF/6-31G**]
TS 4 - 7
TS 3b - 5a
5b
7
7a
H5C3C2O1 = 58.6
H4C3C2O1 = -58.6
C1C2C3O2 = 0.0
C2C3O2H6 = 180.0
H5C3C2O1 = 86.5
H4C3C2O1 = -32.9
C1C2C3O2 = 24.0
C2C3O2H6 = 96.2
C3O2C2O1 = 4.6
H6C3O2C2 = -1.4
H5C3O2H4 = 28.8
H6C3O2H4 = -179.0
C1C2C3O1 = 178.8
C3C2C1H1 = -79.5
C1C2O2H4 = -178.9
C3C2C1H2 = 39.9
C1C2C3H5 = 64.0
C3C2C1H3 = 162.0
C1C2C3H6 = -66.6
C1C2C3O2 = -175.7
C1C2C3H3 = -53.9
O2C3C2O1 = 3.3
H4C1C2O1 = 165.4
C3C2O1H1 = 180.0
H5C1C2O1 = 42.6
C1C2C3H2 = 63.1
H6C1C2O1 = -75.6

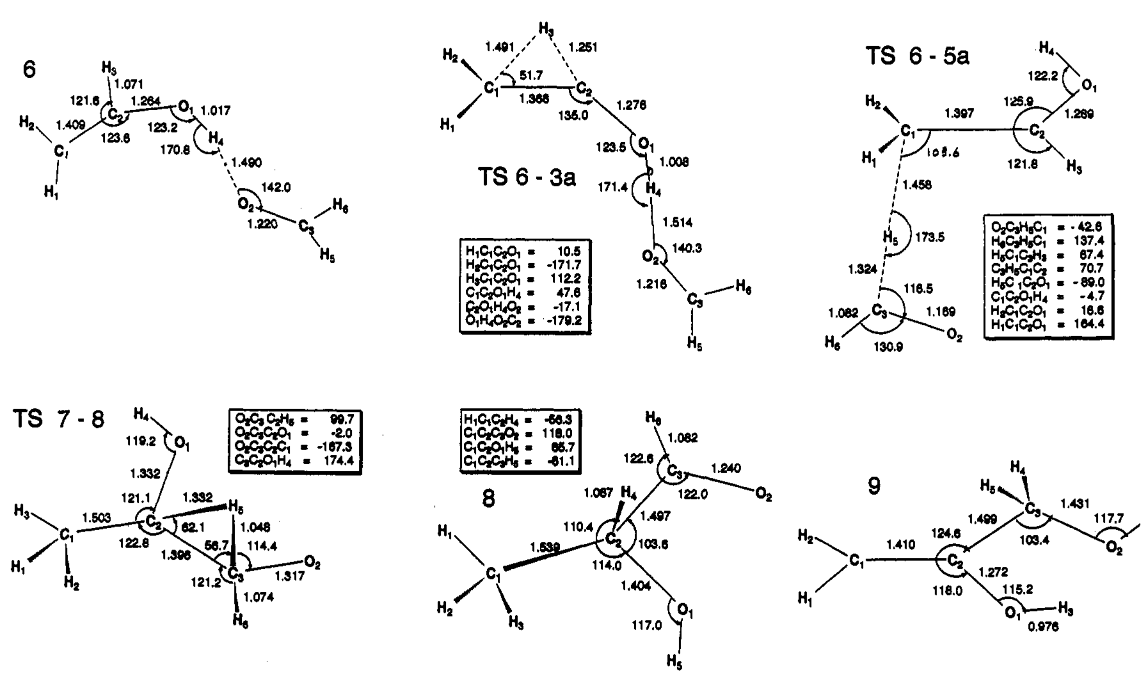
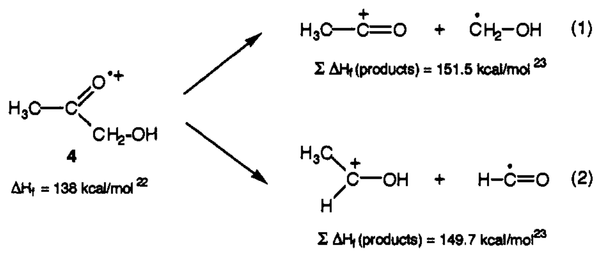


Figure 1. Otimized geometries of (acetol)$^{\bullet +}$ isomers and some transition states. Bond lengths in angstroms, bond angles in degrees.

Scheme 1



sequence **4** → **3a** → **5a** but with either the first or second step taking place at an energy close to the dissociation limit. This mechanism, however, can be tested because it predicts the position of deuterium atoms in the products from labeled precursor molecules, *viz.*

$$\underset{\mathbf{4}\text{-}d_2}{CH_3C(=O)CD_2OH^{\bullet +}} \rightarrow \underset{\mathbf{3a}\text{-}d_2}{[CH_3CO\cdots H\cdots O{=}CD_2]^{\bullet +}} \rightarrow$$

$$\underset{\mathbf{5a}\text{-}d_2}{[CH_3C(D)O\cdots H\cdots O{=}CD]^{\bullet +}} \rightarrow CH_3CDOH^+ + DCO^\bullet$$

and

$$\underset{\mathbf{4}\text{-}d}{CH_3C(=O)CH_2OD^{\bullet +}} \rightarrow \underset{\mathbf{3a}\text{-}d}{[CH_3CO\cdots D\cdots O{=}CH_2]^{\bullet +}} \rightarrow$$

$$\underset{\mathbf{5a}\text{-}d}{[CH_3C(H)O\cdots D\cdots O{=}CH]^{\bullet +}} \rightarrow CH_3CHOD^+ + HCO^\bullet$$

First, the origins of the H atoms in the product ions need to be established. Figure 3 shows the CID mass spectra of $[C_2H_{5-x}D_xO]^+$ (x = 1, 2) ions, all generated from *metastable* precursor ions,[27] namely acetol and ethanol molecular ions and those of isotopomers, and therefore having comparable internal energies as well as common structures.

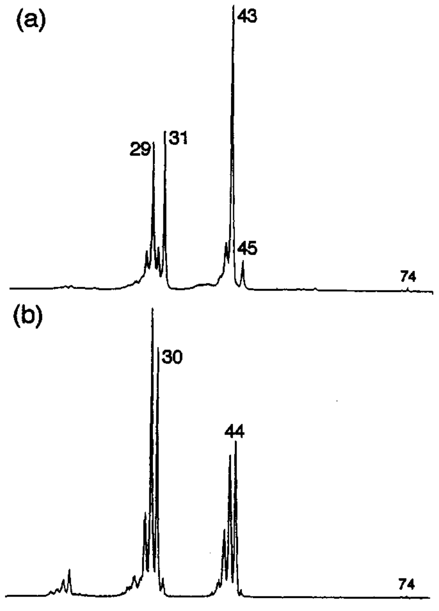


Figure 2. NR mass spectra of (a) $CH_3C(=O)CH_2OH^{\bullet +}$ (**4**) and (b) $[CH_2{=}CH\text{-}O\cdots H\cdots O{=}CH_2]^{\bullet +}$ (**6**).

Figure 3a shows the CID mass spectrum of metastably generated m/z 45 ions from acetol; it is identical with that of the m/z 45 ions of structure CH_3CHOH^+[28] generated from metastable ethanol ions. Figure 3b shows the CID mass spectrum of m/z 46 ions from metastable $[CH_3CD_2OH]^{\bullet +}$, which have the structure $[CH_3CDOH]^+$. This CID mass spectrum is indistinguishable from that of the m/z 46 ions produced from metastable $CH_3C(=O)CH_2OD^{\bullet +}$ (**4**-d). Instead of a process involving keto–enol isomerism, the label has become attached to the carbonyl carbon in the rearrangement of the acetol molecular ion. This is confirmed by the observations in Figure 3c, which illustrates the CID mass spectrum of the m/z 46 ions from metastable $CH_3C(=O)CD_2OH^{\bullet +}$ (**4**-d_2). This spectrum is indistinguishable from that of the m/z 46 ions produced from metastable $[CH_3CH_2OD]^{\bullet +}$. Note the enhanced abundance of m/z 20 relative to m/z 19 and the doubly charged C_2H_3O ion shifting from m/z 21.5 to m/z 22. Thus the loss of $HCO^\bullet$ *cannot* involve the reaction

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[27] Dissociation in the ion source leads to a mixture of isomeric m/z 45 ions, CH_3CHOH^+ and $CH_2{=}CHOH_2^+$, which obscures the analysis of the position of the label in the product ions generated from the D-labeled isotopomers.

[28] Burgers, P. C.; Terlouw, J. K.; Holmes, J. L. *Org. Mass Spectrom.* **1982**, *17*, 369.

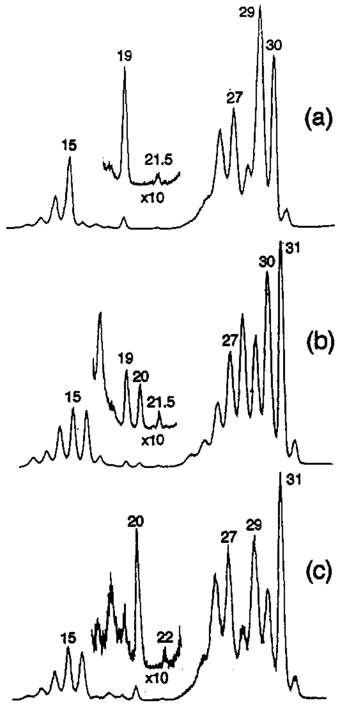
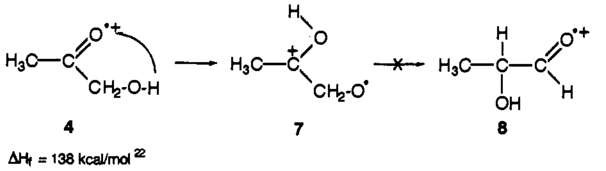


Figure 3. Partial CID mass spectra of product ions from dissociation reactions of metastable ions. (a) $C_2H_5O^+$ from $CH_3C(=O)CH_2OH^{\bullet+}$ (**4**) → $C_2H_5O^+ + HCO^\bullet$. (b) $C_2H_4DO^+$ from $CH_3CD_2OH^{\bullet+} \rightarrow CH_3CDOH^+ + D^\bullet$. (c) $C_2H_4DO^+$ from $CH_3C(=O)CD_2OH^{\bullet+}$ (**4-d$_2$**) → $C_2H_4DO^+ + DCO^\bullet$.

Scheme 2

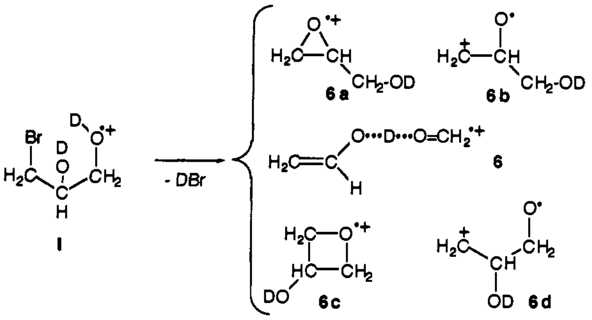


sequence **4** → **3a** → **5a**. Our experimental observations do not necessarily rule out the generation of O···H···O bridged ions **3a**. However, if they are present, they do not, as proposed in the FT-ICR study,[7a,b] further isomerize into **5a** prior to the loss of $HCO^\bullet$.

Our *ab initio* calculations indicate that it is the isomerization step **4** → **3a** which is not feasible. At the Hartree–Fock level of theory, all attempts to locate this TS led to the transfer of the hydroxylic H to the carbonyl group (without a concomitant $C(=O)—C(H_2)$ bond cleavage), yielding the stable distonic ion **7** (Scheme 2, see also Table 1).

Ion **7** has a calculated ΔH_f° value some 9 kcal/mol above that of ionized acetol and is separated from it by only a small barrier. Its formation from **4** represents a "cul-de-sac" isomerization,[29] since **7** cannot dissociate to products of low combined enthalpy either directly or via further rearrangement, the barrier to ionized lactaldehyde (**8**) being too high. It seems likely that this ion, **7**, or its more stable conformer, **7a** (which, however, cannot be directly generated from **4**), is the species recently shown to react by acetyl replacement in the FT-ICR ion–molecule reaction study of ionized acetol.[7a]

Scheme 3



While searching for other $[C_3H_6O_2]^{\bullet+}$ ions produced in the fragmentation of larger species, which could possibly shed some more light on the behavior of ionized acetol, it was observed that 1-bromo-2,3-dihydroxypropane ($BrCH_2CHOHCH_2OH$, **I**) generated a significant *m/z* 74 ion in its normal mass spectrum by the loss of HBr (*m/z* 74, 50% of base peak, *m/z* 44 $[C_2H_4O]^{\bullet+}$). The MI mass spectrum of this $C_3H_6O_2^{\bullet+}$ ion contained an intense peak at *m/z* 45, $[C_2H_5O^+]$ ($T_{0.5}$ = 13 meV), and a weak, narrow *m/z* 44 peak ($T_{0.5}$ = 1.6 meV). In the corresponding CID mass spectrum, *m/z* 44 had become the base peak, with little change in the intensity of *m/z* 45 (now 45%). The CID mass spectrum of the *m/z* 45 ions generated from the *metastable m/z* 74 species was very closely similar to that for metastably produced $[CH_3CHOH^+]$, whereas that of the (CID generated) *m/z* 44 ions is compatible with the $C_2H_4O^{\bullet+}$ isomer ionized vinyl alcohol,[30] $[CH_2{=}CHOH]^{\bullet+}$. The NR mass spectrum is shown in Figure 2b. It displays only a trace recovery peak at *m/z* 74, and the spectrum could result largely from collisional ionization of neutral $CH_2{=}CHOH$ and $CH_2{=}O$ molecules formed upon dissociative neutralization of the parent ion.

The ion $[BrCH_2CHODCH_2OD]^{\bullet+}$ exclusively lost DBr in its normal mass spectrum, and in the *m/z* 46 ions derived from metastable $C_3H_5DO_2^{\bullet+}$, the deuterium was exclusively on oxygen, $[CH_3CHOD^+]$. Similarly, *m/z* 44 $[CH_2{=}CHOH]^{\bullet+}$ was cleanly displaced to *m/z* 45. In the NR spectrum, *m/z* 44 was also cleanly displaced to *m/z* 45, whereas the other peaks were not shifted.

Clearly this *m/z* 74 ion is not ionized acetol, nor does it have anything in common with the dissociation of ionized methyl acetate. On the basis of the above characteristics, the structures shown in Scheme 3 were considered for the product ions.

A simple 1,3 elimination from **I** would produce either ionized glycidol **6a** or its C–O ring-opened form **6b**, whereas the 1,4 elimination would yield 2-hydroxyoxetane ions **6c** or ions **6d**. The experimental ΔH_f° of the $C_3H_6O_2^{\bullet+}$ product ion from **I** was measured to be ≤144 kcal/mol, an upper limiting value.[31] However, the heats of formation of the cyclic product ions **6a** and **6c** are much higher (176 and 164 kcal/mol, respectively[32]), and this precludes their generation from **I**. The same holds for the C–O ring-opened forms **6b** and **6d**, whose ΔH_f values are expected to be even higher than those of their cyclic counterparts.[32] Moreover, metastable glycidol molecular ions **6a** show an

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(29) Hammerum, S.; Vulpius, T.; Audier, H.-E. *Org. Mass Spectrom.* **1992**, *27*, 369.

(30) Terlouw, J. K.; Wezenberg, J.; Burgers, P. C.; Holmes, J. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1121.

(31) From AE (energy-selected electrons) = 10.06 eV (this work), $\Delta H_f(BrCH_2CHOHCH_2OH) = -96.5$ kcal/mol[23a] and ΔH_f HBr = −9 kcal/mol.[23b] However, considering that in the EI mass spectrum the molecular ion is very weak (≤0.1% of base peak *m/z* 125) and that the estimated IE ($BrCH_2CHOHCH_2OH$) is approximately equal to the measured AE (*m/z* 74), the derived ΔH_f (**6**) must be an upper *limiting* value.

(32) The ionization energy (IE) of glycidol, 10.2 eV, combined with its ΔH_f, −59 kcal/mol (from ref 33), gives ΔH_f(**6a**) = 176 kcal/mol. For ionized 2-hydroxyoxetane (**6c**), $\Delta H_f \approx 176$ kcal/mol, from $\Delta H_f((\text{oxetane})^{\bullet+}) = 203$ kcal/mol (ref 23b) and the effect of OH substitution at a non-charge-bearing site (ref 34), −39 kcal/mol, given by $\Delta(\Delta H_f)$ of cyclobutanol and cyclobutane (ref 23b). Ion **6b** will by analogy with similarly ring-opened oxirane (see ref 35) have a considerably higher ΔH_f than the ring-closed form. Consistent with the oxirane results, our calculations on the distonic ion **6b** showed its derived heat of formation also to be far above that estimated for the ring-closed isomer.

(33) Holmes, J. L.; Terlouw, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860.

(34) Holmes, J. L.; Lossing, F. P.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 133.

(35) Nobes, R. H.; Bouma, W.; Macleod, J. K.; Radom, L. *Chem. Phys. Lett.* **1987**, *135*, 78.

Table 2. Estimated and Experimental Heats of Formation (kcal/mol) and Relative Energies (kcal/mol) for Isomers and Components of the (Acetol)$^{\bullet+}$ System

structure	ΔH_f exptl	ΔH_f estd	E_{rel} (exptl/estd)	E_{rel} (theor)[a]
$CH_3C({=}O)CH_2OH^{\bullet+}$ (**4**)	138[b]		0	0
$CH_3C{=}O \cdots H \cdots O{=}CH_2^{\bullet+}$ (**3a**)		138[c,d]	0	−2
$CH_3C(H){-}O \cdots H \cdots O{=}CH^{\bullet+}$ (**5a**)		131[c]	−7	−7
$CH_2{=}CH\text{-}O \cdots H \cdots O{=}CH_2^{\bullet+}$ (**6**)	<144	128[c]	−10	−10
$CH_3CH(OH)C(H){=}O^{\bullet+}$ (**8**)		148[e]	10	12.5
$CH_2{=}C(OH)CH_2OH^{\bullet+}$ (**9**)		122[f]	−16	−17
$CH_3CHOH^+ + HCO^\bullet$	151[g]		13	10
$CH_3CO^+ + CH_2OH^\bullet$	150[g]		12	14
$CH_2{=}CHOH^{\bullet+} + CH_2{=}O$	155[g]		17	15

[a] See Table 1, the complete set of data for the dissociation products is available upon request. [b] This work. [c] Estimate based on the empirical relationship for —O···H···O— proton-bound dimers: SE (kcal/mol) 30.4–0.30, ΔPA (ref 26); SE, stabilization energy relative to the dissociation products of lowest combined enthalpy, PA, proton affinity; appropriate values from ref 23b. [d] From $\Delta H_f(CH_3COOCH_3^{\bullet+})$ (**1**), 139 kcal/mol,[23b] and the calculated energy of ion **3a** relative to **1** as reported in ref 3, one obtains $\Delta H_f(\mathbf{3a})$ = 139 kcal/mol; at the UMP3/6-31G*//UMP2/6-31G* level of theory (Table 1), **4** is 3.1 kcal/mol more stable than **3a**. [e] ΔH_f of the neutral molecule is −84.7 kcal/mol, by additivity[23a] and using −7.5 kcal/mol for C(H)(C)(O)(CO); IE is 0.3–0.4 eV above that of acetol (9.74 eV, this work), cf. IEs of small aldehydes vs analogue ketones in ref 23b. [f] From $\Delta H_f(CH_2{=}C(OH)CH_3^{\bullet+})$, 158 kcal/mol,[23b] and the effect of OH substitution at a non-charge-bearing group,[34] −36 kcal/mol, given by $\Delta(\Delta H_f)$ of propane and *n*-propanol.[23b] [g] From ref 23b.

abundant loss of H_2O in the MI spectrum, a reaction which is absent in the ion formed by HBr loss from **I**.

A route for the HBr loss from **I** that may satisfy the product ion enthalpy constraint involves either a 1,3 or a 1,4 elimination with a concomitant C–C cleavage, leading to the O···H···O hydrogen-bridged ion $[CH_2{=}CHO \cdots H \cdots O{=}CH_2]^{\bullet+}$ (**6**). From our calculations (see Tables 1 and 2), we derived $\Delta H_f^\circ(\mathbf{6})$ = 128 kcal/mol, the same as the estimated value. This species, whose optimized geometry (see Figure 1) is closely similar to that of the extensively studied[8] analogue $[CH_2{=}CHO \cdots H \cdots OH_2]^{\bullet+}$, may readily yield $CH_2{=}CHOH^{\bullet+}$ following collisional excitation, decompose completely upon neutralization into $CH_2{=}CHOH$ and $CH_2{=}O$, and rearrange to yield the thermochemically less-demanding product $[CH_3CHOH^+]$. Our calculations further show that this ion, **6** (Table 1), has the required properties to satisfy the experimental observations—namely no significant energy barriers to the fragmentation products and a high barrier separating it from ion **3a** $[CH_3C{=}O \cdots H \cdots O{=}CH_2]^{\bullet+}$, a key player on the methyl acetate ion's hypersurface. The very small kinetic energy release accompanying the production of $[CH_2{=}CHOH]^{\bullet+}$ is also in keeping with it having the characteristics of a (vinyl alcohol) ion–(formaldehyde) molecule complex at the dissociation threshold, analogous to the previously studied vinyl alcohol/water system.[8]

So far we have been able to rule out several a priori attractive mechanistic possibilities for the loss of $HCO^\bullet$ from metastable acetol ions **4**. It has also become clear that a viable mechanism must satisfy the fate of the D label in the CH_3CHOH^+ product ion. Note that the labeling results also rule out participation of the very stable enol ion $CH_2{=}C(OH)CH_2OH^{\bullet+}$ (**9**, see Table 2). In addition, the CID mass spectra indicated that the majority of the molecular ions retained an acetyl group, and the insensitivity of *m/z* 45 to collision gas indicated that the barrier to rearrangement is not far from the dissociation energy to CH_3CO^+.

Next we considered the possibility, that $HC{=}O^\bullet$ loss from **4** involves the C···H···O bridged species $[CH_3C({=}O) \cdots H \cdots O{=}CH_2]^{\bullet+}$ (**3b**) rather than its O···H···O bridged isomer, **3a**. Our computations show that **3b** is a minimum on the potential energy surface (PES), lying in a (shallow) well, close to the dissociation limits of **4**. Comparison of the geometries (Figure 1) and energies (Table 1) of the two species shows that **3a** differs from **3b** in that the C···H···O bridged ion is less stabilized and that (at the HF level of theory) the bridging H remains close to the C atom. Thus, whereas **3a** has a strong (and rigid)[8] hydrogen bridge, **3b** is a much more loosely bound species akin to the ion–dipole complex $CH_3C(H){=}O^{\bullet+}/CH_2{=}O$. Such species are being increasingly considered as intermediates, and *ab initio* calculations indicate that at low internal energies, ionized acetic acid,[1b] acetamide,[1b] acetone,[1b] formic acid,[36] and also ethylene glycol[6f] all fragment via such complexes.

A 1,5 H shift in **3b** would produce the C···H···O bridged species **5b**, which by direct bond cleavage will dissociate to the observed products. Such a route accounts for the hydroxyl hydrogen being bound to carbon (not oxygen) in the CH_3CHOH^+ fragment ion:

$$\underset{\mathbf{4}\text{-}d_2}{CH_3C(=O)CD_2OH^{\bullet+}} \rightarrow \underset{\mathbf{3b}\text{-}d_2}{[CH_3C(=O) \cdots H \cdots O=CD_2]^{\bullet+}} \rightarrow$$

$$\underset{\mathbf{5b}\text{-}d_2}{[CH_3C(OD) \cdots H \cdots O=CD]^{\bullet+}} \rightarrow CH_3CHOD^+ + DCO^\bullet$$

Ion **3b** may not be directly generated from ionized acetol via a 1,3 H shift and a concomitant C–C cleavage: our calculations indicate that the associated four-membered ring TS (which has a high $\langle s^2 \rangle$ value) lies well above the dissociation limit for loss of $HCO^\bullet$. An energetically feasible route for the formation of ion **3b** involves the participation of ion **4a**, see Figure 1. This ion is a strong (acetyl) ion–(CH_2OH) dipole complex[37] formed by stretching the $C({=}O){-}C(H_2)$ bond in ionized acetol, and rotating the CH_2OH moiety. Elongation of this bond does not immediately lead to dissociation, but it allows the CH_2OH moiety to migrate within the electrostatic field of the acetyl cation, analogous to loss of $OH^\bullet$ from ionized acetic acid.[38] We have not defined TS **4** → **4a**, but from calculations involving a stepwise elongation of the $C({=}O){-}C(H_2)$ bond and concomitant rotation, it appears that this process requires very little energy (~1–2 kcal/mol). That the $C({=}O){-}C(H_2)$ bond in **4** is easily stretched is further indicated by a geometry optimization at the UMP2/6-31G* level of theory: starting from the optimized 4-31 G geometry of its lowest energy conformer (see Figure 1), we arrive at a structure in which the bond length has increased from 1.51 to 1.97 Å. The same calculations were performed on the O···H···O bridged ion **3a**, but here the inclusion of electron correlation does not greatly change the geometry.

Since **4a** is an ion–dipole complex, the CH_2OH moiety can rotate with respect to the acetyl cation[34] and donate the hydroxyl hydrogen to the carbonyl C, via TS **4a** → **3b**. Note, see Table 1, that when electron correlation and ZPVE corrections are included, TS **4a** → **3b** becomes lower in energy than **3b**. Calculations involving electron correlated geometry optimizations (see above) may solve this problem and provide a more refined description of the proposed isomerization steps. Indeed, although the relative energy has not appreciably changed (see Table 1), the MP2 optimized geometry of ion **3b** is more akin to that of TS **4a** → **3b** than the HF optimized structures for **3b** (see Figure 1). However, we do not expect that such post-HF computations, which become prohibitively expensive for this system of relatively large ions, will change the overall picture.

Ion **3b** lies close to the thermochemical threshold for formation of $CH_3CHOH^+ + HC{=}O^\bullet$ (see Tables 1 and 2) but well below the dissociation limit for direct bond cleavage into $CH_3C(H){=}O^{\bullet+} + CH_2{=}O$, by 32 kcal/mol.[23b] The ion can be viewed as an (acetaldehyde) ion–(formaldehyde) dipole complex, and rotation

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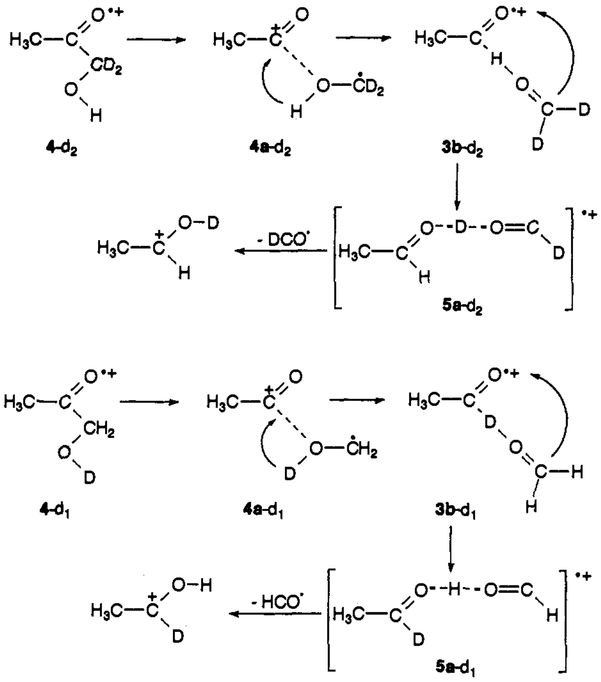
(36) Ruttink, P. J. A.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *113*, 23.

(37) For recent reviews, see: (a) Longevialle, P. *Mass Spectrom. Rev.* **1992**, *11*, 157. (b) Morton, T. H. *Org. Mass Spectrom.* **1992**, *27*, 353.

(38) Heinrich, N.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *79*, 295.

Scheme 4



of the dipole, the $CH_2{=}O$ moiety, with respect to the ion, $CH_3C(=O)H^{•+}$, is expected to require little energy.[1b] If the C···H···O bond would remain intact during this rotation, a 1,5 H shift would give ion **5b**, a stable minimum on the PES (see Table 1) which may serve as a precursor for direct bond cleavage to CH_3CHOH^+ + $HC{=}O^•$. However, in the search for the TS describing this transformation, we located a TS, TS **3b** → **5a**, which indicates that the CH···O bond breaks upon rotation and H transfer. TS **3b** → **5a** lies below the dissociation limit, and the coordinate of its imaginary frequency does indeed correspond to H transfer from the $CH_2{=}O$ group to the carbonyl O atom.[39] Note, see Figure 1, that this TS suggests the formation of an O···H···C bridged species, $[CH_3C(H)O \cdots H \cdots C(H){=}O]^{•+}$ (**5c**), rather than the O···H···O bridged ion $[CH_3C(H)O \cdots H \cdots O{=}CH]^{•+}$ (**5a**). However, ion **5c**, if it exists as a stable minimum at all, does not seem to be accessible from this TS: when the O–H bond is shortened and the H–C bond is simultaneously lengthened along the reaction coordinate, the species appears to oscillate over a flat energy surface close to the dissociation limit until, upon reorientation of the $HC{=}O^•$ dipole, the stable O···H···O bridged species **5a** is reached. Note that, analogous to the behavior of ion **3a** in the dissociation chemistry of methyl acetate, the very stable ion **5a** is generated at energies close to the dissociation limit for the loss of $HCO^•$, and thus in the dissociation chemistry of acetol it represents a transient intermediate only.

In summary, the mechanistic picture that emerges from these computations and which satisfies all of our experimental observations involves two consecutive hydrogen transfers in ionized acetol akin to reactions of $CH_2OH^•$ with the acetyl ion and of formaldehyde with ionized acetaldehyde (Scheme 4).

One final point remains to be addressed: can we exclude the recent proposal based on an FT-ICR study[7a,b] that the O···H···O bridged isomer **3a** plays a role in the gas-phase ion chemistry of ionized acetol? First, our MS/MS/MS experiments on the D-labeled acetol isotopomers leave no doubt that metastable ions **4** do *not* dissociate via **3a**. Moreover, our calculations indicate (see above) that transfer of the hydroxylic H atom to the carbonyl group in covalently bound **4** yields the distonic ion **7**, not **3a**. On the other hand, the calculations also indicate that **4** can easily adopt the configuration of an ion–dipole complex, **4a**, and it could be argued that this species could serve as the precursor to **3a**. This is problematic in view of the extensive computational study by Heinrich et al.[3] on the methyl acetate ion PES. In this study, a minimum structure was found akin to our ion **4a**, but with a considerably shorter ion–dipole distance (see structure **7** in Chart 1 of ref 3). Such an ion, **4b**, was also found as a minimum in our study: it lies somewhat higher in energy than **4a** and is connected to it via a low-lying TS **4a** → **4b**, thus indicating that, upon ionization, acetol can access a flat PES characterized by ion–dipole complexes. In the above study, the isomerization sequence **4b** → $[CH_3C(OH)OCH_2]^{•+}$, **2** → **3a** was examined, but the calculated barrier was found to lie far above the experimentally established energy level for dissociation into $CH_3C{=}O^+$ + $^•CH_2OH$.

The work of Heinrich et al.[3] also provides a plausible rationalization as to why the acetyl ion and $^•CH_2OH$ dipole components in **4a**/**b** would not easily interact to form the O···H···O bridged isomer **3a**. It was found that a continuous lengthening of the $CH_3C{=}O \cdots HOCH_2$ bond in **3a** results in a charge distribution which leads to $CH_3C{=}O^•$ + $^+CH_2OH$ rather than the more stable products $CH_3C{=}O^+$ + $^•CH_2OH$. The dissociation leading to the correct products can occur from the excited state ($^2A''$) of **3a**. This state has the correct charge distribution, and it is "symmetry correlated" with the products $CH_3C{=}O^+$/$^•CH_2OH$, but it lies much higher in energy, roughly 20 kcal/mol above the electronic ground state $^2A'$. These findings indicate that the recombination of the $CH_3C{=}C^+$ and $^•CH_2OH$ components in **4a** to the O···H···O bridged isomer **3a** requires too much energy to compete with rearrangement to the C···H···O bridged species **3b** proposed in our mechanism. This intriguing point clearly warrants further investigation using higher levels of theory than those practical at the time of the study by Heinrich et al. We also note that in the ion–molecule chemistry of ionized acetol, an acetyl *radical* displacement reaction is proposed[7b] which would be in keeping with the presence of a structure having the charge distribution of ground-state ions **3a**. However, if a facile isomerization **4** → **3a** does occur, it must be a cul-de-sac with regard to the low-energy dissociation of ionized acetol into CH_3CHOH^+ and $HCO^•$.

Acknowledgment. The authors gratefully acknowledge that appearance energies have been measured by Dr. F. P. Lossing. J.L.H. and J.K.T. thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. J.K.T. thanks Dr. P. C. Burgers, Professor H. I. Kenttämaa, Dr. D. Schröder, and Professor H. Schwarz for stimulating discussions.

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[39] This TS probably represents the barrier for the transformation **3b** → **5a**, although analysis of the IRC calculation of this TS and the nature of the imaginary frequency provides no direct evidence for rotation of the $CH_2{=}O$ group concomitant with the H transfer. Note that the energy of this TS is slightly lower than that of ion **3b**. A reviewer has rightly pointed out that this emphasizes that the optimized geometry of ion **3b** shown in Figure 1 may represent only one of many configurations accessible to the dissociating ions and that the second H can be transferred via a range of geometries around **3b**–**5a**.