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(66) Carried out using optimized geometries for $CSH_3^+$ (Table III), affixing a standard-geometry[67] methyl group in place of H in each isomer. For $CH_3CH{=}SH^+$, the methyl was assumed to eclipse the C—S bond, was found to be slightly more stable syn to SH than anti, and was affixed with a CC distance of 1.484 Å (STO-3G value in $C_2H_5^+$);[61] this gave $E = -470.661\,77$ hartrees. For $CH_3CH_2{-}S^+$ triplet, methyl was affixed staggering the CS bond at a CC distance of 1.54 Å;[67] this gave $E = -470.689\,33$ hartrees. It was necessary to specify the electronic configuration in the initial guess to obtain this energy. Singlet $CH_3CH_2{-}S^+$ at a similar geometry was found to lie ~60 kcal/mol higher than this triplet.
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# Collisional Activation and Theoretical Studies of Gaseous $COH_3^+$ Ions[1]

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**Abstract:** Collisional activation spectra of $m/z$ 31 ions from a variety of precursors are consistent with a single isomeric structure, $H_2C{=}OH^+$. However, reexamination of published data combined with ab initio calculations indicates a shallow energy minimum for a second structure, a $C_{2v}$ complex of $H_2$ and $HCO^+$, heat of formation ($\Delta H_f$) 194 vs. 165 kcal/mol for $H_2C{=}OH^+$. The triplet ground state methoxy ion, $H_3C{-}O^+$, is calculated to be unstable, $\Delta H_f = 231$ kcal/mol.

In the preceding paper[2] collisional activation (CA) mass spectra and ab initio calculations showed that two isomers of $CSH_3^+$, protonated thioformaldehyde ($H_2C{=}SH^+$) and thiomethoxy ion ($H_3C{-}S^+$), are stable in the gas phase, with the latter higher (~10 kcal/mol) in energy. To elucidate further the relative abilities of oxygen and sulfur for carbocation

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**Table I.** Collisional Activation Spectra of $COH_3^+$ Ions

| compd | *m/e* 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|
| $CH_3OH$ | 15 | 25 | 35 | 1.1 | 4 | 14 | 8 |
| 20 eV[a] | 15 | 24 | 35 | 1 | 4 | 14 | 8 |
| $C_2H_5OH$ | 15 | 24 | 35 | 1.0 | 5 | 15 | 7 |
| 13 eV | 14 | 28 | 31 | 1 | 4 | 16 | 6 |
| $CH_3CH_2CH_2CH_2OH$ | 15 | 23 | 35 | 1.0 | 5 | 14 | 8 |
| $HOCH_2CH_2SH$ | 15 | 25 | 37 | 1.0 | 5 | 12 | 7 |
| $HCOOCH_3$ | 16 | 25 | 33 | 0.9 | 5 | 14 | 6 |
| $CH_3COOCH_3$ | 16 | 26 | 32 | 1.0 | 6 | 13 | 7 |
| 19 eV | 16 | 24 | 34 | 1 | 6 | 14 | 6 |
| $C_2H_5OC_2H_5$ | 16 | 22 | 33 | 0.9 | 6 | 16 | 7 |
| $CH_3OCH_3$ | 15 | 25 | 34 | 0.9 | 4 | 15 | 7 |
| 17 eV | 15 | 24 | 33 | 1 | 4 | 15 | 8 |
| $CH_3SOCH_3$ | 15 | 24 | 24 | 1.5 | 6 | 14 | 6 |
| $CH_3OCH_2OCH_3$ | 13 | 23 | 37 | 1.3 | 5 | 15 | 7 |

[a] Ionizing energy; in unspecified cases 70 eV was used.

stabilization, the isomeric $COH_3^+$ ions a and b are investigated in a similar fashion in this paper. Previous CA studies of

$$\begin{array}{ccc} H_2C{=}\overset{+}{O}H & H_3C{-}\overset{+}{O} & H_2\cdots HCO^+ \\ \text{a} & \text{b} & \text{b}' \end{array}$$

$C_2OH_5^+$ and $C_3OH_7^+$ isomers found no evidence for stable alkoxy ions, $R_1R_2CH\text{-}O^+$,[3,4] but similar studies of $C_2SH_5^+$ and $C_3SH_7^+$ concluded that the corresponding thioalkoxy isomers are not stable either.[5] There is some indication from appearance potential (AP) studies[6-8] that b is capable of existence; recent monoenergetic electron measurements of Lossing[8] indicate that the heat of formation ($\Delta H_f$) of b is $\leq 192$ (the data curve was extremely "tailed"), vs. 165 kcal/mol for $\Delta H_f$(a).[9] Gas-phase equilibrium measurements by Hiraoka and Kebarle[10] on ions prepared by the equation

$$HCO^+ + H_2 = H_3CO^+ \qquad (1)$$

give $\Delta H_f = 194$ kcal/mol;[11] these ions were found to be stable only below $-100$ °C, $\Delta H$ (eq 1) = $-3.9$ kcal/mol.[10] These values led to the proposal that b is a loose complex of $H_2$ and $HCO^+$, b′.[10,12] Bowen and Williams[13] also give evidence that b ions formed from $CH_3ONO_2$ and $CH_3OCH_3$ are of low stability, with decomposition to $HCO^+$ predominating over isomerization to a. An alternative to their rationalization of the high barrier for b → a has recently been proposed by Schleyer, Jemmis, and Pople,[14] whose preliminary ab initio MO calculations on b "indicate that bound species exist, but with rather low interaction energies".

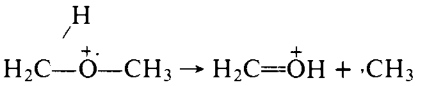
## Experimental Section

Data were obtained as described in the preceding paper.[2] For the CA spectra of *m/e* 31 ions all observed peaks are reported except *m/e* 29 and 30, which correspond to metastable transitions, and *m/e* 28, whose much larger relative abundance (an order of magnitude greater than that of *m/e* 14) was the same within a larger experimental error for all spectra of the compounds studied.

## Experimental Results and Discussion

All CA spectra of *m/e* 31 ions from a variety of oxygen-containing compounds (Table I) were found to be the same within experimental error, consistent with the existence of only one ion structure $\sim 10^{-5}$ s after ion formation. This isomer should be the more stable protonated formaldehyde, $H_2C{=}OH^+$ (a), based on the negligible $CH_3^+$ abundance. $[CH_3^+]/[CH_2^+]$ is 0.03, even lower than the value of 0.1 for the CA spectrum of $H_2C{=}SH^+$ (for $H_3C{-}S^+$ this value is >1).[2] For the $H_2C{=}SH^+$ spectrum the abundances of $S^+$ and $SH^+$ ions are greater than those of $O^+$ and $OH^+$ in the Table I spectra, reflecting the higher stability of the sulfur ions ($\Delta H_f$, kcal/mol:[15] $S^+$, 306; $O^+$, 374; $SH^+$, 274; $OH^+$, 308). The maximum proportion of the $H_3C\text{-}S^+$ isomer was formed from $CH_3SSCH_3$ using 18-eV electrons; repeated CA measurements of $COH_3^+$ ions formed from $CH_3OCH_3$ at a variety of intermediate electron energies failed to give any evidence for b formation.

As observed by Bowen and Williams,[13] the normal mass spectrum (70-eV electrons) of $CH_3OCH_3$ shows a low value of $[COH_3^+]/[CHO^+]$, indicating that most b ions of higher internal energies decompose by the reverse of reaction 1, and do not isomerize b → a. We find that lowering the electron energy to 20 eV produces a sixfold *increase* in this ratio, corresponding to an increase in the relative yield of the a isomer. Similar behavior was observed for $H_2C{=}SH^+$ formed by displacement,[2,5] suggesting eq 2 as the chief pathway for the formation of a ions from $CH_3O$-containing compounds (Table I).



$$H_2C{-}\overset{+\cdot}{O}{-}CH_3 \rightarrow H_2C{=}\overset{+}{O}H + {\cdot}CH_3 \qquad (2)$$

**Thermochemical Studies.** Appearance potential studies of *m/e* 31 ions from several methoxy compounds have indicated a wide variety of $\Delta H_f$(b) values.[6-8,15] This is not surprising in light of the observation (Table I) that such ions are actually of structure a, probably formed by eq 2. This mechanism could account for the extremely "tailed" data curve reported by Lossing,[8] with this $\Delta H_f$ value of $\leq 192$ kcal/mol referring to a, not b, ions. Thus $\Delta H_f(b) = 194$ kcal/mol[11] appears to be the most reliable experimental value available.

## Theoretical Results and Discussion

Previous theoretical studies of $COH_3^+$ ions have addressed questions such as barriers to rotation and inversion,[16] resonance energy,[17] and force constants[18] of a, and the proton affinity of $H_2C{=}O$.[19] Of greater interest to the present study are papers[20-23] dealing with the relative energies of a and b ions; however, none has investigated both singlet and triplet forms, and no data are available on b′.[14] Table II summarizes results of published ab initio calculations[23] and ours carried out at the same level of approximation (STO-3G and 4-31G).

**$H_2C{=}OH^+$.** All calculated and assumed geometries of a are in general agreement, indicating an unsymmetrical planar structure.[16,20-23] The CO bond length (STO-3G, 1.271 Å;[23] double $\zeta$ optimization, 1.260 Å;[20] but MINDO/3, 1.222 Å)[21] is intermediate between those of $H_2C{=}O$ (1.217 Å, STO-3G)[23] and $H_3COH$ (1.433 Å).[23] Population analysis and calculated rotation barriers also indicate substantial CO $\pi$ bonding in a.[16] Most calculations (except one)[20] show the $CH_2$ group tilted in the molecular plane, with the HCO angle syn to OH as the larger; this distortion is presumably due to steric effects.

**$H_3C\text{-}O^+$.** The ground state of b is a triplet ($^3A_1$) of $C_{3v}$ symmetry. As in $H_3C\text{-}S^+$,[2] the bond distance to the heteroatom in b is long: STO-3G gives 1.534 Å, in poor agreement with another minimal basis determination of 1.72 Å.[22] Both studies agree, however, on the presence of increased s character at carbon relative to $sp^3$, indicated by longer CH bonds and larger HCH angles than in ethane. The picture which emerges is of a relatively loose complex between $CH_3^+$ and O; at 4-31G, the energy difference between $H_3C\text{-}O^+(^3A_1)$ and $CH_3^+ + O(^3P)$ is only 22 kcal/mol.[23]

One calculation (MINDO/3) has been reported for singlet b,[21] but $C_{3v}$ symmetry was enforced. At STO-3G, singlet ($^1A'$)$H_3C\text{-}O^+$ was optimized assuming $C_s$ symmetry; it is found to contrast with the triplet in having a shorter CO distance (1.440 Å) and two long (1.117 Å) CH bonds bent toward oxygen (MINDO/3 gives 1.224 and 1.141 Å, respectively).[21] These features are characteristic of hyperconjugative interaction between the formally vacant p orbital on O and two of

**Table II.** Theoretical Energies and Geometries of $COH_3^+$ Isomers

| ion | symmetry | state | total energy, hartrees (rel energy, kcal/mol) STO-3G | total energy, hartrees (rel energy, kcal/mol) 4-31G | geometry[a] |
|---|---|---|---|---|---|
| $H_2C{=}OH^{+\,b}$ | $C_s$ | $^1A'$ | −112.707 02<br>(0) | −113.974 86<br>(0) | CO = 1.271, OH = 1.003, $CH_1$ = 1.114,[c] $CH_2$ = 1.114, COH = 114.7, $OCH_1$ = 123.0, $OCH_2$ = 116.4 |
| $H_3C{-}O^{+\,b}$ | $C_{3v}$ | $^3A_1$ | −112.699 61<br>(4.6) | −113.912 07<br>(3.94, 65.8[d]) | CO = 1.534, CH = 1.103, OCH = 104.3 |
| $H_3C{-}O^+$ | $C_s$ | $^1A'$ | −112.565 57<br>(88.8) | −113.793 53<br>(113.8) | CO = 1.440, $CH_1$ = 1.100,[e] $CH_2$ = 1.117, $OCH_1$ = 111.0, $OC(H)_{23}$ = 112.6, $H_2CH_3$ = 106.4 |
| $H_2{\cdots}HCO^+$ | $C_{2v}$ | $^1A_1$ | −112.624 15<br>(52.0) | −113.902 92<br>(45.1) | CO = 1.138, $CH_1$ = 1.133,[e] $H_2H_3$ = 0.716, $H_1{\cdots}(H)_{23}$ = 2.058 |
| $H_2 + HCO^+$ | | $^1\Sigma^+$ | (52.9) | (46.9) | |

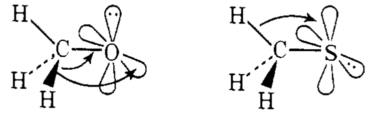
[a] Optimized at STO-3G. Bond lengths in ångstroms, angles in degrees. [b] From ref 23. [c] $H_1$ syn, $H_3$ anti to OH. [d] 4-31G energy corrected empirically assuming the energy of the formal "spin-flip reaction" $CH_3{-}O^+(^3A_1) + CH_2(^1A_1) = CH_2(^3B_1) + CH_3{-}O^+(^1A')$ to be given correctly at 4-31G; see ref 2. [e] $H_2$, $H_3$ symmetry equivalent. $(H)_{23}$ refers to the midpoint of a line from $H_2$ to $H_3$.

**Table III.** Theoretical Heats of Formation for $COH_3^+$

| no. | reaction | reaction energy[a] | $\Delta H_f°(COH_3^+)$[b] |
|---|---|---|---|
| 1 | $CH_2{=}OH^+ + CH_4 = CH_3OH + CH_3^+$ | 47.8 | 183 |
| 2 | $+ CH_3CH_3 = CH_3OH + CH_3CH_2^+$ | 17.9 | 173 |
| 3 | $+ CH_3NH_2 = CH_3OH + CH_2NH_2^+$ | −45.5 | 181 |
| 4 | $+ H_2 = CH_3^+ + OH_2$ | 16.9 | 186 |
| | | | av 181 ± 6 |
| 5 | $CH_3{-}O^{+\,c} + CH_4 = OH^{+\,d} + CH_3CH_3$ | 40.7 | 263 |
| 6 | $+ NH_3 = OH^+ + CH_3NH_2$ | 46.5 | 265 |
| 7 | $+ OH_2 = OH^+ + CH_3OH$ | 48.3 | 268 |
| 8 | $+ CH_3^+ = OH^+ + CH_3CH_2^+$ | 10.8 | 253 |
| 9 | $+ HOOH = HOO^{+\,e} + CH_3OH$ | 28.4 | 217 |
| | | | av 253 ± 21 |

[a] kcal/mol, calculated using 4-31G energies from ref 23. [b] kcal/mol, calculated by combining the theoretical reaction energy with experimental heats of formation (as ref 11 and 15). [c] $^3A_1$ state (reactions 5–9). [d] $^3\Sigma^-$ state (reactions 5–8). [e] $^3A''$ state.

the CH bonds. Such interaction occurs also in singlet $H_3C{-}S^+$ but involves only one CH bond. The oxygen system is evidently



able to take fuller advantage of this interaction owing to the shorter distances involved and the higher electronegativity of the vacant p orbitals. Despite the similarity between this $CH_3{-}O^+$ structure and the MINDO/3 transition state for $H_2$ loss from a,[21] this STO-3G minimum is stable with respect to all distortions as long as $C_s$ symmetry is maintained.

**$H_2{\cdots}HCO^+$.** Bringing $H_2$ toward the H end of $HCO^+$ results in a bound complex b of $C_{2v}$ symmetry, with a distance of 2.058 Å between the formyl H and the midpoint of $H_2$. Calculations on such a complex were mentioned by Schleyer et al.,[14] but details were not reported. As in the analogous sulfur system,[2] a complex of slightly higher energy exists with the configuration $H_2{\cdots}OCH^+$.

**Relative Energies.** Both levels of theory indicate a to be the lowest energy isomer, and agree fairly well on the relative energy of $H_2{\cdots}HCO^+$ (b′), which is given at 4-31G to lie 2 kcal/mol below separated $H_2 + HCO^+$ and 45 kcal/mol above a. The corresponding experimental values are 4,[10] in good agreement, and 29 kcal/mol, which is substantially lower; however, with such a weakly bound complex optimization at a higher level of theory will often lead to a substantially different geometry and lower energy.[24]

The singlet state of b is found to be 114 kcal/mol above a at 4-31G, 89 kcal/mol at STO-3G; the true value is likely to be intermediate. It is evident that singlet $H_3C{-}O^+$ is too high in energy to play a role in the observed gas-phase chemistry. Although the triplet b is clearly lower than this, and higher in energy than a, the present calculations do not provide a definitive answer for the latter difference. This is found to be only 5 kcal/mol at STO-3G, but 39 kcal/mol at 4-31G; correcting the latter for correlation energy differences[2] leads to our final estimate of 66 kcal/mol. Haney et al.[22] report values of 8.6 kcal/mol using a minimal basis and 34.0 kcal/mol at the double ζ level, comparable to the STO-3G to 4-31G trend. Adding configuration interaction (CI), a method which should take correlation energy into account, to the minimal basis increases the energy by 22 kcal/mol, compared to the 27 kcal/mol increase in the 4-31G value from this correction. However, Haney et al.[22] prefer to cite the double ζ value as their best estimate.

As in the accompanying paper,[2] we have also calculated heats of formation for a and triplet b by employing a series of isodesmic reactions, evaluating the reaction energies theoretically and combining these with the necessary $\Delta H_f$ values (Table III). Trends among cation stabilization energies (reactions 1–3) involving a are similar to those found for $H_2C{=}SH^+$; OH adjacent to $C^+$ is more stabilizing than H or $CH_3$, but not as much as $NH_2$. Averaging results from these comparisons with that from a hydrogenation reaction (4) gives $\Delta H_f°(a)$ = 181 kcal/mol.

Triplet b is compared in reactions 5–9 with other triplet ions $OH^+$ and $OOH^+$, giving $\Delta H_f°(b)$ = 253 kcal/mol. The energy difference between isomers a and b is 72 kcal/mol, in good agreement with the empirically corrected 4-31G value of 66 kcal/mol in Table II. In keeping with the sulfur study,[2] we choose the latter value, yielding $\Delta H_f(b)$ = 231 kcal/mol. Williams and co-workers have shown[13] that rearrangement b → a requires at least 13 kcal/mol more energy than this; on the other hand, dissociation to $HCO^+ + H_2$ would be exothermic by 33 kcal/mol.[11] Our failure to observe stable b ions from methoxy precursors such as $CH_3OCH_3$ (Table I) is consistent with a low activation energy for this dissociation and with the unfavorable steric requirements for the exothermic rearrangement of such precursor ions to form the marginally stable isomer $H_2\cdots HCO^+$.

**Charge Stabilization, O vs. S.** In the previous paper[2] it was demonstrated that $\pi$ bonding in $H_2C{=}SH$ is slightly more effective than that in a. A similar comparison of triplet b and $H_3C\text{-}S^+$ ($\Delta H_f$ = 215 kcal/mol)[2] gives $\Delta H$(eq 3) = −59 kcal/mol. Clearly, a sulfur atom is much better suited to accommodating positive charge than oxygen, owing to the larger, more polarizable orbitals on sulfur. This appears to be the major factor responsible for the observed differences between gas-phase organosulfur and -oxygen cations.

$$H_3C{-}O^+ + CH_3SH \rightarrow CH_3OH + H_3C{-}S^+ \qquad (3)$$

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# Ferric Ion Sequestering Agents. 3. The Spectrophotometric and Potentiometric Evaluation of Two New Enterobactin Analogues: 1,5,9-*N,N′,N″*-Tris(2,3-dihydroxybenzoyl)cyclotriazatridecane and 1,3,5-*N,N′,N″*-Tris(2,3-dihydroxybenzoyl)triaminomethylbenzene[1]

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**Abstract:** The complexation and protonation equilibria of the ferric complexes of 1,5,9-*N,N′,N″*-tris(2,3-dihydroxybenzoyl)cyclotriazatridecane (3,3,4-CYCAM) and 1,3,5-*N,N′,N″*-tris(2,3-dihydroxybenzoyl)triaminomethylbenzene (MECAM) have been investigated by potentiometric and spectrophotometric techniques. Proton dependent metal-ligand equilibrium constants $[K^* = ([ML][H]^3)/([M][H_3L])]$ have been determined to be log $K^*$ = 9.5 and 3.4 for the ferric complexes of MECAM and CYCAM, respectively. These results have been used to estimate the normal formation constants as $10^{46}$ for ferric MECAM and $10^{40}$ for ferric CYCAM. The MECAM value is the largest formation constant of any synthetic iron chelator. Both complexes undergo a series of protonations which shift the mode of bonding from one involving coordination through the two phenolic oxygens of the dihydroxybenzoyl group (catecholate mode) to one in which the iron is coordinated to the carbonyl oxygen and the ortho phenolate group (salicylate mode). The results are discussed in relation to the chelation therapy of chronic iron overload, as occurs in the treatment of Cooley's anemia.

While iron is an essential element for growth in all living things and is needed in relatively large amounts in man (approximately 4 g of the element are in the average adult),[2] it is also very toxic when present in excess. In its acute form, iron overload (usually from the ingestion of iron supplement preparations by infants) constitutes one of the most common types of accidental poisoning.[3] In its chronic form, iron overload results as a side effect of the transfusion therapy of genetic disorders such as $\beta$-thalassemia major (Cooley's anemia) and related diseases.[3]

In searching for new ligands to be used in iron chelation therapy, one initial approach has been the examination of naturally occurring iron chelating agents. In microorganisms, the acquisition of iron usually involves the synthesis and excretion of low-molecular-weight ligands which show both a high affinity and a high specificity for ferric ion.[4,5] These li-

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