The heats of formation of some C₂H₅O⁺ isomers, relevant bond energies in ethanol and PA(CH₃CHO)

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The ionization potentials of the transient species CH₂CH₂O, CH₃CHOH, and CH₃CH₂OH (generated by the F+ethanol reactions) are measured by photoionization mass spectrometry: I.P.(CD₂CD₂O)=10.29±0.08 eV (tentative), I.P.(CH₃CHOH)<6.85 eV, and I.P.(CD₂CH₂OH) ≤8.35±0.06 eV. The latter results in a cation of uncertain structure. These reactions also generate vinyl alcohol (adiabatic I.P.=9.33±0.01 eV) and acetaldehyde. A redetermined appearance potential of CH₂CHOH⁺ from ethanol enables one to infer the proton affinity of acetaldehyde to be ≥183.8±0.2 kcal/mol and an α (C–H) bond energy in ethanol >91.1 kcal/mol (0 K). The appearance potential of m/e=45 ion from bromoethanol is interpreted as formation of a C₂H₅O⁺ isomer having the oxirane structure, with ΔHᵢ₀ of ~173.9 kcal/mol, consistent with earlier alternative measurements. A second increase in the m/e=45 ion yield curve from ethanol is interpreted as formation of this same isomer. This interpretation, and an alternative cycle, lead to a β (C–H) bond energy in ethanol of 98±2 kcal/mol. The implication of the current results to the dynamics of dissociation of ethanol cations is discussed. © 1994 American Institute of Physics.

I. INTRODUCTION

There is obvious current interest in ethanol as a fuel. Among its combustion products, one may anticipate various isomers involving loss of a H atom. These include

C₂H₅OH → CH₃CHOH+H, (1)
C₂H₅OH → CH₃CH₂OH+H, (7)
C₂H₅OH → CH₃CHOH+H, (3)

Alfassi and Golden¹ obtained D₂₉₈=93.0±1.0 kcal/mol for reaction (1); this value has been maintained in a 1982 review² and in a 1988 compilation.³ It corresponds to ΔHᵢ₀(CH₂CHOH) = -15.2±1.0 kcal/mol. For reaction (3), Ervin et al.⁴ obtained D₀=103.1±0.9 kcal/mol (D₂₉₈=104.6±0.8) kcal/mol, which corresponds to ΔHᵢ₀(CH₂CH₂O) = -0.4±0.9 kcal/mol [ΔHᵢ₀(CH₂CH₂O) = -3.7±0.8 kcal/mol] by combining a measured gas phase acidity with a measured electron affinity of CH₂CH₂O. To our knowledge, the dissociation energy of reaction (2) is not known. Hintsan et al.⁵ and Specter and Hess⁶ studied the 193 nm laser photodissociation of chloro-, bromo-, and iodoethanol, which generate CH₂CH₂OH with various internal energies, but the bond energy, and hence ΔHᵢ₀(CH₂CH₂OH), could not be determined in these experiments. Tully⁷ has demonstrated the importance of CH₂CH₂OH in combustion and atmospheric chemistry as the initial product in the reaction of OH with C₂H₄.

The heats of formation of the radical cations of these species are also of interest. An accurate heat of formation of CH₃CHOH⁺ would establish the proton affinity of acetaldehyde, a quantity which is in current dispute,⁸ and is an important peg in the ladder of proton affinities. Since CH₃CHOH⁺ is believed to be the first fragment in the photodissociative ionization of ethanol, its appearance potential should provide the desired result. At least two such measurements have been reported in prior investigations. These will be examined and we shall try to improve upon them.

One of the oddities of earlier investigations of the ion with m/e=45 resulting from dissociative ionization of ethanol is that there appear to be two energy regions where the ion yield increases—one near threshold (~10.8 eV) and the other at ~11.7–12.0 eV. This has been observed in electron⁹ and photon impact,¹⁰ by charge exchange,¹¹ and by photoion–photoelectron coincidence spectroscopy.¹² The higher energy increase appears to be contradictory to the strong form of quasiequilibrium theory. We shall provide some experimental results which may help to rationalize this behavior.

The CH₃CH₂O⁺ cation is not expected to be observed upon dissociative ionization of ethanol, since its appearance potential is likely to be at so high an energy that further dissociation and/or rearrangement probably occur. This expectation is analogous to the difficulty of observing CH₂O⁺ from dissociative ionization of methanol, where the lower energy CH₂OH⁺ fragment dominates. However, it is possible to deduce the heat of formation of CH₃CH₂O⁺ if one can measure the ionization potential of CH₃CH₂O. A recent study by Bogan and Nesbitt¹³ offers some hope that the ionization potentials of the three radicals represented in reactions (1)–(3) can be determined. These authors studied the reaction of F atoms with C₂D₅OH. They concluded that about 50% of H(D) abstraction resulted in formation of the ethoxy radical, with the remainder roughly split between CH₂CH₂OH and CH₃CHOH (or their deuterated forms). Thus, using this reaction and suitable isotopic tagging, it should be possible to measure these three I.P.s. If the heat of formation of CH₂CH₂OH⁺ could be determined in a separate experiment, one could then, in principle, infer the missing dissociation energy corresponding to reaction (2). Toward this end, we examined the photodissociation ionization of BrCH₂CH₂OH, which presumably would form
CH$_2$CH$_2$OH$^+$ + Br. These proposed experiments and their results are discussed below.

II. EXPERIMENTAL ARRANGEMENT

The transient species CD$_3$CD$_2$O, CH$_3$CHOH, and CD$_2$CH$_2$OH were prepared in situ by reaction of F atoms with CD$_3$CD$_2$OH, ordinary ethanol, and CD$_2$CH$_2$OH, respectively. The fluorine atoms were generated in a microwave discharge through pure F$_2$. The description of the flow tube and reaction cup has been given previously, as has the photoionization mass spectrometric method. CD$_2$CH$_2$OH, CH$_3$CH$_2$OD, and bromoethanol were obtained from Aldrich Chemical Company, while CD$_2$CD$_2$OH was from Cambridge Isotope Laboratories. The isotopic purity, as stated by the manufacturer, was 99.5 at.% D for CH$_3$CH$_2$OD, 99 at.% D for CD$_2$CH$_2$OH, and 98 at.% D for CD$_3$CD$_2$OH.

III. EXPERIMENTAL RESULTS

A. The heat of formation of CH$_2$CHOH$^+$

The threshold region of the photoion yield curve of m/e =45 ions from ethanol is displayed in Fig. 1 on a photon energy scale. The isomeric form of m/e=45 is presumed to be CH$_3$CHOH$^+$ because it is the lowest energy isomer and its formation from CH$_2$CH$_2$OH$^+$ involves a simple bond cleavage. It is also the lowest energy fragment. Hence its threshold, properly interpreted, should represent not just an upper limit to $\Delta H_f^0$(CH$_2$CHOH$^+$), but a number close to the true value of this quantity.

The smooth curve drawn through the data points is the best fit of a linear kernel function convoluted with a thermal broadening function. The thermal broadening function was evaluated using Haarhoff's expression for the rovibrational state density $p$. Two forms were evaluated—the first, in which all 21 vibrations were treated as such, and the other in which the two lowest frequencies, which are hindered rotors, were treated as free rotors. The vibrational frequencies were taken from Gurvich et al. The detailed evaluation of the broadening functions is given in the Appendix. Two types of kernel functions, representing the idealized 0 K fragmentation behavior, were examined—a linear function $\phi(E-E_f)=c(E-E_f)$ and an exponential function $\phi(E-E_f) = c[1-e^{-b(E-E_f)}]$, where $E_f$ is the threshold energy. Only slight differences were observed by the least-squares criterion and in the visual observation of the quality of the various fits to the data. In all of the attempted fits, the data points in the exponentially tailing region lie slightly above the fitted functions. The average result for the 0 K threshold is 10.801 ± 0.005 eV. This is arrived at by correcting the shift deduced from the artificial temperature which appears in the broadening function (see the Appendix) by the true average internal energy at 298 K (0.0819 eV). When combined with $\Delta H_f^0$(C$_2$H$_5$OH) = −51.88 ± 0.03 kcal/mol (Ref. 17), and $\Delta H_f^0$(H) = 51.633 kcal/mol, this threshold yields $\Delta H_f^0$(CH$_2$CHOH$^+$) ≤ 145.6 ± 0.1 kcal/mol.

For purposes of comparison, the 0 K threshold given by Refae and Chupka was 10.78±0.02 eV. Brehm et al. did not quote a threshold value from their photoelectron–photoion coincidence spectrum. Our reading of their Fig. 9 yields 10.73±0.02 eV which becomes 10.81±0.02 eV after applying the internal energy correction.

B. The heat of formation of CH$_2$CH$_2$OH$^+$

Our initial attempt to determine the heat of formation of this isomeric form utilized CD$_3$CH$_2$OH as the precursor. The expectation was that the photoion yield curve of CD$_3$CH$_2$OH$^+$ would differ from that of CD$_3$CHOH$^+$, and that the threshold for the former would provide a basis for arriving at $\Delta H_f^0$(CH$_3$CH$_2$OH$^+$).

The result was that the photoion yield curve of m/e =47 (nominally CD$_3$CH$_2$OH$^+$) was essentially the same as m/e =48 (CD$_3$CHOH$^+$), but m/e =47 was much weaker, about 1/40 the intensity of m/e =48. This measurement encompassed an energy range from threshold (~10.8 eV) to 13.5 eV, i.e., well beyond the second increase in the m/e=45 curve from ethanol observed previously and in the current research. The implication is that H–D scrambling has occurred in the parent ion prior to dissociation, but that there is a large isotope effect favoring the departure of a H, rather than a D atom.

Earlier work provides some support for these observations. Harrison and co-workers used isotope labeling to examine the decomposition of (C$_2$H$_5$O)$^+$ to both (H$_2$O)$^+$ and C$_2$H$_7$+. They concluded that “the reaction involves a mechanism in which the hydrogen originally bonded to oxygen is retained in the oxygen containing fragment, while the four hydrogens originally bonded to carbon become indistinguishable.” We infer that the same behavior occurs for C$_2$H$_6$O$^+$ ions decomposing to C$_2$H$_3$O$^+$ fragments. The large isotope effect observed here is similar to that postulated by Keyes and Harrison (k$_{H/D}=1.30$) favoring transfer of H from carbon to oxygen in the reaction

$[C_2(H,D)_3O]^+-[(H,D)_3O]^++C_2(H,D)_2].$

The second attempt to determine $\Delta H_f^0$(CH$_3$CH$_2$OH$^+$) was based on bromoethanol (BrCH$_2$CH$_2$OH) as a precursor.
PHOTON ENERGY (eV) PHOTON ENERGY (eV)

FIG. 2. The photoion yield curve of CH$_2$OH$^+$ from bromoethanol. The smooth curve drawn through the data points is the best fit of a linear kernel function convoluted with a thermal broadening function appropriate for bromoethanol. The sloping line is the kernel function, displaced to its hypothetical position at 0 K.

FIG. 3. The photoion yield curve of m/e = 45 ion from bromoethanol. The smooth curve is the best fit of a linear kernel function convoluted with the same thermal broadening function used in Fig. 2. The sloping line is again the hypothetical 0 K fragmentation function.

Since C–Br bonds are typically ~30 kcal/mol weaker than C–H bonds, it was anticipated that the first fragment following photodissociation of bromoethanol would be CH$_2$CH$_2$OH$^+$ (+Br). If the heat of formation of bromoethanol were well established, the threshold for this photodissociative ionization process could conceivably lead to $AH_f^0$(CH$_2$OH$^+$). Unfortunately, $AH_f^0$(BrCH$_2$CH$_2$OH) is not known experimentally; it has only been estimated.\(^3\) It can be inferred if we measure the appearance potential of an alternative dissociation process of bromoethanol, where the heats of formation of the products are known. It turns out that a strong fragmentation process, which also involves a simple bond cleavage, is the reaction

$$\text{BrCH}_2\text{CH}_2\text{OH} + hv \rightarrow \text{CH}_2\text{OH}^+ + \text{CH}_2\text{Br} + e. \quad (4)$$

One of the products CH$_2$OH$^+$ has a well-established heat of formation 171.6±0.2 kcal/mol (Ref. 20) at 0 K. The value of $AH_f^0$(CH$_2$Br) is less certain. Tschuikow-Roux and collaborators\(^{21,22}\) have arrived at $AH_f^0$(CH$_2$Br) = 40.4 ± 1.0 kcal/mol based on an analysis of thermochemical and kinetic data. If we accept this result, it is equivalent to $AH_f^0$(CH$_2$Br) = 42.9 ± 1.0 kcal/mol.

1. $AH_f^0$(CH$_2$OH$^+$/BrCH$_2$CH$_2$OH) and $AH_f^0$(BrCH$_2$CH$_2$OH)

The photoion yield curve of CH$_2$OH$^+$ from bromoethanol is presented in Fig. 2. The smooth curve drawn through the data points is based on the Haarhoff function for the rovibrational density of states of bromoethanol convoluted with a linear kernel function, as was done for ethanol (see the Appendix). The functional form of the approximated density of states function is the same as for ethanol, but with different artificial temperatures of 443.07 (case 1) and 419.06 K (case 2), as discussed in the Appendix. In this fit, the data points follow the calculated curve far into the exponential tail. There is only a slight deviation between the results from cases (1) and (2) and between linear and exponential kernel functions. The average result for the 0 K threshold is 11.314 ±0.005 eV based on a calculated average rovibrational internal energy of 0.099 eV at 298 K. The vibrational frequencies of bromoethanol were taken from Thomassen et al.\(^2\) From this threshold, and the aforementioned $AH_f^0$(CH$_2$OH$^+$) and $AH_f^0$(CH$_2$Br), one can compute $AH_f^0$(BrCH$_2$CH$_2$OH) ≥ −46.4 ± 1 kcal/mol.

2. $AH_f^0$(CH$_2$CH$_2$OH$^+$)$/\text{BrCH}_2\text{CH}_2\text{OH}$ and $AH_f^0$(BrCH$_2$CH$_2$OH$^+$)$/$

The photoion yield curve of m/e = 45 ion from bromoethanol is shown in Fig. 3 together with the same convoluted Haarhoff function used in Sec. II B 1 above. The fitted function lies slightly below the data points in the exponential tail region. We do not yet have sufficient experience with this behavior to be able to attribute the deviation to experimental conditions (e.g., some contribution by collision-induced dissociation) or to a lack of understanding of the underlying assumptions. In the present study, we have seen two examples of deviation, both being first fragments, and one example of an essentially perfect fit, which was not a first fragment.

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The quality of the fit was almost independent of kernel function (exponential or linear) and of the vibrational cases (21 or 19 vibrations) for this fragment. The average result for the 0 K threshold is 10.774±0.005 eV. This corresponds to the reaction

$$\text{BrCH}_2\text{CH}_2\text{OH} + hv \rightarrow [(\text{CH}_2\text{CH}_2\text{OH})^+] + \text{Br} + e. \quad (5)$$

By combining this threshold with $AH_f^0$(Br) = 28.18 kcal/mol (Ref. 17) and $AH_f^0$(BrCH$_2$CH$_2$OH) obtained in Sec. II B 1, we deduce $AH_f^0$[(CH$_2$CH$_2$OH$^+$)] ≈ 173.9 kcal/mol. In principle, the thresholds for reactions (4) and (5) are both upper limits. In the evaluation of $AH_f^0$[(CH$_2$CH$_2$OH$^+$)], they tend to partially cancel, although the magnitude of the deviation between true threshold and upper limit is not known. In addition, the uncertainty of $AH_f^0$(CH$_2$Br) must be retained, and hence the result must remain approximate.
C. The transient species C₂H₅O, CH₂CHOH, and CH₂CH₂OH

In order to selectively study these isomers, isotopic samples were utilized.

1. Photoion yield curve of C₂H₅O

Initially, the reaction of F atoms with C₂H₅OD was employed. According to Bogan and Nesbitt, about 50% of the hydrogen abstraction reactions should yield C₂H₅O, with the remaining 50% shared between CH₃CH₂OD and CH₃CHOH. The latter would appear at $m/e = 46$ upon photoionization, whereas the desired C₂H₅O should be observable at $m/e = 45$.

Figure 4(a) is the photoion yield curve observed at $m/e = 45$ during this abstraction experiment. Steplike structure is apparent. The first indication of a significant signal (half-rise of first step) occurs at 1329±2 Å = 9.33±0.01 eV. To check on this observation, F atoms were reacted with C₂D₂OH, and the photoion yield curve of $m/e = 50$ (C₂D₂O⁺) was examined. The resulting spectrum (vide infra) was quite different. There was no sign of a threshold at ~1329 Å. Consequently, another interpretation for Fig. 4(a) was sought.

Phenomenologically, Fig. 4(a) involves a loss of 2 amu from the precursor C₂H₅OD, which can result from a loss of D or two H atoms. In other abstraction reactions studied in our laboratory, we have often observed successive H atom loss, e.g., PH and P formation from PH₃, SiH₂ from SiH₃, and SiH₄ and even SiH₂ from SiH₄. Loss of two H atoms from C₂H₅OD could generate CH₂=CHOH (vinyl alcohol) or CH₂CD(O) (acetaldehyde). The adiabatic ionization potential of CH₂=CHOH has been determined to be 9.30±0.05 eV, whereas that of acetaldehyde is 10.2291±0.0007 eV. Hence, vinyl alcohol appeared to be a plausible progenitor of the spectrum in Fig. 4(a). This hypothesis was tested by reacting F atoms with ordinary ethanol (C₂H₅OH) and monitoring the $m/e = 44$ peak (parent 2 amu).

The resulting photoion yield curve, shown in Fig. 4(b), matches that in Fig. 4(a) quite well. The adiabatic ionization potential (9.33±0.01 eV) is within the error bounds found for vinyl alcohol by photoelectron spectroscopy (9.30±0.05 eV) and the steps in the photoion yield curve occur at intervals of 1400±50 cm⁻¹, matching the vibrational frequency of CH₂=CHOH observed in the photoelectron spectrum.

This ionization potential is significantly higher than the value (9.14 eV) initially reported by electron impact spectroscopy, but closer to subsequent electron impact values 9.22±0.03 eV (Ref. 30) and 9.26±0.1 eV (Ref. 31).

At higher photon energies, the onset for photoionization of acetaldehyde was readily observed, indicating that this species is also formed in the abstraction reactions (see Sec. III C 3 below).

In order to avoid contamination from other reaction products, the isotopic variant C₂D₅OH was then chosen as reactant. Here, C₂D₅O⁺ from C₂D₅O will appear at $m/e = 50$, while CD₂CD(OH), CD₂CD₂OH, vinyl alcohol, and acetaldehyde will appear at lower masses. However, the bulk of the C₂D₅OH, which remains unreacted, can generate a background at $m/e = 50$ in two ways:

- Mass leakage from parent ionization (~0.5% of parent ion intensity)
- An isotopic impurity in the sample (CD₂CHOH and CHD₂CD₂OH)

Both of these background sources exist prior to reaction with F atoms. Hence, the operating procedure was to measure the relative photoion yields at $m/e = 51$ and $m/e = 50$ before the abstraction reaction and again during the abstraction reaction. In this way, it was possible to subtract the unwanted impurity at $m/e = 50$, providing the net photoion yield curve shown in Fig. 5.

One sees a relatively steep onset at ~1150 Å (10.78 eV) and a shallower slope toward longer wavelength, with an onset at ~1205±10 Å (10.29±0.08 eV), more apparent in the enlarged inset. The higher energy threshold is suspiciously close to that for the first fragment from ethanol (see Fig. 1), although such a contribution should have been removed by the subtraction process. In addition, this first fragment from CD₂CD₂OH should be CD₂CD(OH)⁺, appearing at a lower ($m/e = 49$) mass than that represented by Fig. 5.

Bogan and Nesbitt also examined the F+C₂D₅OH reaction, but with electron impact ionization. They observed an increase in the $m/e = 50$ ion peak of ~15%-20% with the fluorine discharge on, compared to discharge off, using 70 eV electrons. In our experiment, we observe a 25%-30% increase (discharge on-discharge off) at $m/e = 50$ using 11.4
eV photons. Interestingly, they found that their detection sensitivity for \( \text{C}_2\text{D}_5\text{O} \), relative to \( \text{C}_2\text{D}_3\text{OH} \), decreased from 70 eV to a minimum at -12 eV, and then increased again to 9 eV. However, at energies below the IP of \( \text{C}_2\text{D}_3\text{OH} \) (-10.47 eV), this ratio should become infinite and is not meaningful.

They did not attempt to infer an ionization potential for \( \text{C}_2\text{D}_2\text{O} \). If we assume that the photoion yield curve of Fig. 5 is to be attributable entirely to the process \( \text{C}_2\text{D}_2\text{O} + h\nu \rightarrow \text{C}_2\text{D}_2\text{O}^* \), then we are forced to conclude that adiabatic ionization at 10.29 eV is a weak process, and a much stronger one begins at \( \sim 10.78 \) eV. The weak onset may be related to the minimum in detection sensitivity observed by Bogan and Nesbitt.

An adiabatic I.P. of 10.29 eV, when combined with the low energy window at \( m/e = 45 \) consequent upon ionization of \( \text{CH}_3\text{CHOH} \), makes a determination of the true adiabatic I.P. difficult.

### 3. Photoion yield curve of \( \text{CH}_2\text{CH}_2\text{OH} \)

In order to selectively photoionize this isomer, \( \text{CD}_2\text{CH}_2\text{OH} \) is chosen as reactant. The desired species \( \text{CD}_2\text{CH}_2\text{OH} \) should generate \( m/e = 47 \) ions observed during the fluorine atom abstraction reactions with \( \text{CD}_2\text{CH}_2\text{OH} \) is shown in Fig. 7. One sees a dramatic increase in the ion yield curve at \( \sim 1210 \) Å, corresponding approximately to the adiabatic ionization potential of acetaldehyde. However, weaker ionization persists to longer wavelength. Upon higher amplification (Fig. 7), this weaker ionization manifests a more-or-less linear decline between \( \sim 1350 - 1485 \) Å, and perhaps lower. Thus, the adiabatic I.P. of \( \text{CD}_2\text{CH}_2\text{OH} \) is \( \lesssim 8.35 + 0.06 \) eV, and perhaps \( \lesssim 8.18 \) eV. The implication of the monotonically increasing ion yield curve is that a relatively large change in geometrical structure accompanies ionization.

All of the appearance potentials and ionization potentials measured in the present study are summarized in Table I.

It is instructive to compare the directly measured I.P.(\( \text{CD}_2\text{CH}_2\text{OH} \)) with estimates based on our measured \( \Delta H^0_{f/0}[(\text{CH}_2\text{CH}_2\text{OH})^+] \approx 173.9 \) kcal/mol obtained in Sec. III B 2. We consider first the case of bromoethanol. The C-Br bond energy in \( \text{CH}_3\text{Br} \) and \( \text{C}_2\text{H}_5\text{Br} \) is 69.5 \pm 0.3 and 69.3 \pm 0.5 kcal/mol at 0 K. If we transfer such a bond energy to \( \text{BrCH}_2\text{CH}_2\text{OH} \), we deduce \( \Delta H^0_{f/0}(\text{CH}_2\text{CH}_2\text{OH}) = -5.5 \pm 2 \) kcal/mol and hence I.P.(\( \text{CH}_2\text{CH}_2\text{OH} \)) would be
Smith and Radom\textsuperscript{8} have recently calculated 
P.A.\(\text{(CH}_3\text{CHO}) = 184.1\text{ kcal/mol at the G2 level. They point out a discrepancy between their calculated value and earlier experimental values} [\text{P.A. = 185.7 (Ref. 31) and 186.6 kcal/mol (Ref. 3)}]\text{ based on proton transfer equilibria and proton transfer reactions. The present result is seen to be in excellent agreement with the calculated value.}

### IV. INTERPRETATION OF RESULTS

#### A. The proton affinity of acetaldehyde

This quantity is defined as the negative of the exothermicity for the reaction

\[
\text{CH}_3\text{CHO} + \text{H}^+ \rightarrow \text{CH}_3\text{CHOH}^+ \]

at 298 K. We have determined \(\Delta H^0_{f_{298}}(\text{CH}_3\text{CHOH}^+) \leq 145.6 \pm 0.1\text{ kcal/mol. To correct this quantity to 298 K, we once again assume that} (H_{298} - H_0) \text{ CH}_3\text{CHOH}^+ \text{ lies midway between that of CH}_3\text{CHO and CH}_3\text{CH}_2\text{OH. This adjustment results in} \Delta H^0_{f_{298}}(\text{CH}_3\text{CHOH}^+) \pm 0.2\text{ kcal/mol. The quantities} \Delta H^0_{f_{298}}(\text{CH}_3\text{CHO}) = -39.6 \pm 0.1\text{ kcal/mol and} \Delta H^0_{f_{298}}(\text{H}^+) = 365.7\text{ kcal/mol are firm literature values.}^3 \text{ Therefore,}\ P.A.\text{(CH}_3\text{CHO}) \geq 183.8 \pm 0.2\text{ kcal/mol. Although this is rigorously a lower limit, it is very likely close to the true value, since it is based on an appearance potential of a first fragment resulting from a simple bond cleavage.}

#### B. The heats of formation and structures of \text{C}_2\text{H}_5\text{O}^+ isomers

In an earlier calculation from Radom’s laboratory, by Nobes et al.,\textsuperscript{15} the relative energies and structures of 16 possible \text{C}_2\text{H}_5\text{O}^+ isomers were calculated at the third-order Möller–Plesset (MP3)/6-31G** level. The lowest energy (most stable) isomer was, as expected, \text{CH}_3\text{CHOH}^+. The next most stable \text{H}_2\text{C}-\text{O}-\text{CH}_2^+ \text{ is unlikely to be formed in the current experiments, but could be determined using dimethyl ether as a target.}^32 \text{ This is followed by} \text{CH}_3=\text{CH}-\text{OH}^+, \text{also unlikely to be generated in our experiments. The fourth and fifth isomers in order of stability were estimated to be} 7.78 \pm 0.1\text{ eV. Alternatively, if we transfer the C–H bond energy from ethane to H–\text{CH}_2\text{CH}_2\text{OH in ethanol, we infer an I.P.} (\text{CH}_2\text{CH}_2\text{OH}) \text{ of} \sim 7.7\text{ eV. Both of these values are significantly lower than the directly measured value. We shall probe the implications of this discrepancy in the next section.}

### TABLE I. Appearance and ionization potentials (in eV, at 0 K).

<table>
<thead>
<tr>
<th>Process</th>
<th>Threshold</th>
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<tbody>
<tr>
<td>\text{CH}_3\text{CHOH} \rightarrow \text{CH}_3\text{CHOH}^+ + \text{H}^+ e \text{ or ions}</td>
<td>10.801 \pm 0.005</td>
</tr>
<tr>
<td>\text{BrCH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHOH}^+ + \text{CH}_2\text{Br} + \text{e}</td>
<td>11.314 \pm 0.005</td>
</tr>
<tr>
<td>\text{Na}^+\text{H}_2\text{O} \rightarrow [\text{CH}_3\text{CHOH}^+] + \text{Na}^+ + \text{e}</td>
<td>10.774 \pm 0.005</td>
</tr>
<tr>
<td>\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CHOH}^+ + \text{e}</td>
<td>10.29 \pm 0.08^*</td>
</tr>
<tr>
<td>\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CHOH}^+ + \text{e}</td>
<td>8.65</td>
</tr>
<tr>
<td>\text{CD}_2\text{CHOH} \rightarrow [\text{CD}_3\text{CHOH}^+] + \text{e}</td>
<td>8.35 \pm 0.06</td>
</tr>
<tr>
<td>\text{CD}_2\text{CHOH} \rightarrow [\text{CD}_3\text{CHOH}^+] + \text{e}</td>
<td>8.18 \pm 0.08^*</td>
</tr>
</tbody>
</table>

* Tentative.

The heat of formation of the species we have been labeling [(\text{CH}_3\text{CHOH}^+)?] is found to be \(\sim 28.3 \pm 1\text{ kcal/mol above} \text{CH}_3\text{CHOH}^+. \text{This degree of excitation is seen to be rather close to that of the cyclic structure and correspondingly very different from that of the calculated} \text{CH}_3\text{CH}_2\text{OH}^+. \text{On this basis, we are forced to conclude that in the dissociative ionization of} \text{BrCH}_2\text{CH}_2\text{OH, the lower energy cyclic form of} \text{C}_2\text{H}_5\text{O}^+ \text{ is formed.}

Solka and Russell\textsuperscript{33} had come to this conclusion earlier in their study of electron impact ionization of bromoethanol. They inferred the heat of formation of the \textit{m/e = 45} ion from bromoethanol to be \(166 \pm 1\text{ kcal/mol, about 26 kcal/mol higher than their value for the ground state structure (CH}_3\text{CHOH}^+)\text{. They were guided in their interpretation by a prior study performed by Beauchamp and Dunbar.}^34 \text{ These latter authors studied the reaction}

\[
\text{CH}_3\text{CHO}^+ + \text{BrCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} \rightarrow \text{BrCH}_2\text{CH}_2\text{OH}^+ \text{ + ions} \]

using ion cyclotron resonance. Beauchamp and Dunbar found that this reaction "proceeds in both directions at thermal ion energies, implying that the reaction is very nearly thermoneutral," and concluded that the heat of formation of protonated ethylene oxide was \(170 \pm 4\text{ kcal/mol. Although Solka and Russell obtained} 10.47 \pm 0.05\text{ eV for their appearance potential of} \textit{m/e = 45} \text{ ion from bromoethanol (cf. 10.774 \pm 0.005 eV in the present work), and the value of} \Delta H^0 \text{ (bromoethanol)} \text{ used was not stated, their inference regarding the isomeric form of} \text{C}_2\text{H}_5\text{O}^+ \text{ concurs with ours. If this is the}
case, it cannot be expected that the thermochemical cycle involving \( A.P.(CH_2CH_2OH^+/BrCH_2CH_2OH) \), \( I.P.(CH_2CH_2OH) \), and \( D_a(\text{Br-CH}_2\text{CH}_2\text{OH}) \) will be closed. The \( I.P.(CH_2CH_2OH) \) presumably refers to a linear structure, whereas the \( A.P.(\text{CH}_2\text{CH}_2\text{OH}^+/\text{BrCH}_2\text{CH}_2\text{OH}) \) may refer to a cyclic structure. If we use our estimated \( \Delta H_f^{0}(CH_2CH_2OH) \) and the measured \( I.P.(CH_2CH_2OH) \), we arrive at \( \Delta H_f^{0}(\text{CH}_2\text{CH}_2\text{OH}^+) \), which is about 38-41 kcal/mol above \( CH_3CHOH^+ \), still not as high as the calculated value for such a structure, but considerably closer.

This state of affairs raises some interesting questions. It will be recalled that the photoion yield curve of \( CH_3CHOH \) in Fig. 7 appeared to gradually approach the background level. Can Fig. 7 represent a superposition of photoionization from \( CH_2CH_2OH \) to linear \( CH_2CH_2OH^+ \), with strong Franck-Condon factors, and to the cyclic structure, with weak Franck-Condon factors? According to Nobes et al., \( CH_3CHOH^+ \) is already strongly bent, with a \( C-C-O \) bond angle of about 109°. Bending in this coordinate can approach the cyclic structure.

In the Introduction, we discussed the unexpected second increase in the \( m/e = 45 \) ion in the dissociative ionization of ethanol at 11.7-12 eV observed in several experiments. This is about 0.9-1.2 eV, or 21-28 kcal/mol, above the threshold for \( CH_3CHOH^+ \) from ethanol, which is just the energy range we have surmised for the excitation of the cyclic structure above \( CH_3CHOH^+ \). If the dissociative ionization of bromoethanol gives rise to the cyclic structure, might there not be a second dissociative ionization of ethanol itself involving a \( C=\text{H} \) bond on the terminal carbon, also giving rise to this structure? We shall return to this question in Sec. IV C below.

Nobes et al.\(^{13} \) found that the ethoxy cation did not represent a local minimum in the \( C_2H_5O^+ \) surface. Apparently, they did not consider the triplet ethoxy cation. In the methanol case, \( CH_2O^+ \) was found to be a metastable triplet, both by calculation\(^{35} \) and experiment.\(^{36} \) Curtiss et al.\(^{37} \) have now reexamined this problem and found that triplet \( C_2H_5O^+ \) does indeed have a local minimum. Their calculated \( I.P.(C_2H_5O) \) to this triplet state is 10.32 eV, in excellent agreement with our tentative experimental onset of 10.29±0.08 eV.

Williams and Hamill\(^{39} \) obtained \( I.P.(C_2H_5O) = 9.11 \) eV by electron impact ionization of ethoxy radical generated by pyrolysis of \( C_2H_5ONO \). In hindsight, this could conceivably have been some other pyrolysis product, e.g., \( CH_3NO \), rather than ethoxy radical. They also inferred \( \Delta H_f^{0}(C_2H_5O) \) by the method of "breakology," i.e., looking for discontinuities, presumed to manifest themselves as linear segments, in an appearance potential curve of \( C_2H_5O^+ \) from various precursors. For \( C_2H_5ONO \) as precursor, the onset was attributed to \( C_2H_5O^++NO^- \) (10.34 eV) and the first break to \( C_2H_5O^++NO \) (11.19 eV). This implied \( E.A.(NO) = 0.85 \) eV, in apparently excellent agreement with the value \( E.A.(NO) = 0.89 \) eV available at that time. The current value for \( E.A.(NO) = 0.89 \) eV is 0.026±0.005 eV.\(^{39} \) Alternative values for \( \Delta H_f^{0}(C_2H_5O^+) \) found by Williams and Hamill came from still higher breaks in the appearance potential curves from \( C_2H_5O \) and \( CH_3OH \). Their average value for \( \Delta H_f^{0}(C_2H_5O^+) \) was 9.15 eV=211 kcal/mol (presumably re-ferring to 298 K) and hence \( \Delta H_f^{0}(C_2H_5O^+) \approx 214 \) kcal/mol. Our current value is \( \Delta H_f^{0}(C_2H_5O^+) \approx 237 \) kcal/mol and presumably refers to the triplet state of the cation.

The heats of formation of these isomeric ions are compared with \( ab\) \( initio \) calculated values and other experimentally inferred values in Table II.

### C. The \( C=\text{H} \) and \( O=\text{H} \) bond energies in ethanol

Since the ethoxy cation cannot be observed in the photodissociative ionization of ethanol, the photoionization method utilizing the \( A.P./I.P. \) combination is thwarted. The value obtained recently by Ervin et al.\(^{4} \) using the negative ion cycle \([D_a(\text{CH}_3\text{CH}_2\text{O}-\text{H})=103.1\pm0.9 \text{kcal/mol] is an acceptable alternative.} \)

For the \( (C=\text{H}) \) bond energy, we subtract \( I.P.(\text{CH}_3\text{CHOH}) < 6.85 \) eV from \( A.P.(\text{CH}_3\text{CHOH} / \text{ CH}_3\text{OH}) = 10.801\pm0.005 \text{ eV to yield } D_0(\alpha=\text{CH})\geq 3.95 \text{ eV=91.1 kcal/mol. This apparently supports, but does not improve upon } D_0(\alpha=\text{CH}) = 91.3\pm1.0 \text{ kcal/mol inferred from } D_{298} = 93.0\pm1.0 \text{ kcal/mol given by Alfassi and Golden.} \)

These latter authors measured an activation energy for the reaction \( I+\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHOH}+\text{HI}, \) and assumed a reverse activation energy of \( 1\pm1 \text{ kcal/mol. In the late 1980's, Gutman and co-workers}^{40} \) were able to directly measure the activation energy for a number of \( R+\text{HI} \) reactions.

### Table II. Heats of formation of some \( C_2H_5O^+ \) isomers (in kcal/mol at 0 K)

<table>
<thead>
<tr>
<th>Species</th>
<th>Present results</th>
<th>( ab) ( initio ) calculations</th>
<th>Other experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_4CHOH^+ )</td>
<td>114.5±0.1</td>
<td>145.4(^{a} )</td>
<td>146±3(^{b} ), 142(^{c} )</td>
</tr>
<tr>
<td>( OH )</td>
<td>( ~173.9 )(^{d} )</td>
<td>( 174.5 )(^{d} )</td>
<td>172±3(^{b} )</td>
</tr>
<tr>
<td>H(_2)C(_2)OH</td>
<td>( ~157 )±2(^{e} )</td>
<td>196.8(^{f} )</td>
<td>192(estimated)(^{g} )</td>
</tr>
<tr>
<td>( CH_3CHO^+ )</td>
<td>( ~237 )(^{h} )</td>
<td>Unstable(^{d} )</td>
<td>214(^{h} )</td>
</tr>
</tbody>
</table>

\(^{a} \)From Ref. 8 either using G2 energies directly, or from their \( A.P. \)(\( CH_3\text{CHOH} \)). To arrive at \( \Delta H_f^{0}(\text{CH}_3\text{CHOH}^-) \), we use \( \Delta H_f^{0}(\text{CH}_3\text{CHOH}) = -37.0\pm0.1 \text{ kcal/mol and } \Delta H_f^{0}(\text{H}^-) = 365.2 \text{ kcal/mol from Ref. 3} \)

\(^{b} \)From Refs. 34 and 42 corrected to 0 K.

\(^{c} \)From Ref. 3 corrected to 0 K.

\(^{d} \)From Ref. 37

\(^{e} \)From A.P.\((\text{CH}_3\text{CHO})/\text{bromoethanol}) \), after initially determining \( \Delta H_f^{0}(\text{Br-CH}_2\text{CH}_2\text{OH}) = -46.4\pm1 \text{ kcal/mol and assuming that the cyclic cation is formed.} \)

\(^{f} \)From Ref. 15 and footnote a, above; it is not clear whether this is a minimum on the potential energy surface.

\(^{g} \)From I.P.(\( CH_3\text{CH}_2\text{OH} \))=8.33±0.06 \text{ eV and } D_0(\text{H-CH}_2\text{CH}_2\text{OH})=98±2 \text{kcal/mol.} \)


\(^{i} \)From \( \Delta H_f^{0}(\text{C}_2\text{H}_5\text{O}) \) given by Ervin et al. (Ref. 4) and \( I.P.(\text{C}_2\text{H}_5\text{O}) = 10.29±0.08 \text{ eV, the current tentative result.} \)

\(^{j} \)Nobes et al. (Ref. 15) find that \( C_2H_5O^+ \) "does not represent a local minimum," but they may have neglected to study the triple surface.

\(^{k} \)Reference 38, corrected to 0 K. Note that this result is based on a very questionable interpretation of data.
and concluded that they were negative and as low as \(-2\) kcal/mol. If this correction is applicable to the HI+CH$_3$CHOH reaction, its effect would be to increase the bond energy given by Alfassi and Golden by 1–3 kcal/mol.

In this context, we note that Curtiss et al.$^{37}$ have calculated $D_0(\alpha{-}CH)=94.9$ kcal/mol. If we accept 1830 Å=6.78 eV in Fig. 6 as the adiabatic I.P. of CH$_3$CHOH, then our experimental $D_0(\alpha{-}CH)$ becomes 92.8 kcal/mol, which is just about within the uncertainty of the ab initio calculation.

To arrive at the $\beta$ (C–H) bond energy, we have devised two independent arguments. It will be recalled that $\Delta H_f^0(\text{BrCHCH$_2$OH})$ was deduced to be \(-46.4\pm1\) kcal/mol from the A.P.(CH$_3$OH/BrCHCH$_2$OH). Now consider the dissociation reactions

$$\text{BrCHCH$_2$OH} \rightarrow \text{CH$_2$CHOH} + \text{Br} \quad (6)$$

and

$$\text{HCl} + \text{Cl$_2$OII} \rightarrow \text{ClCl} + \text{OII} \quad (7)$$

Let $x$ be the heat of formation of CH$_3$CHOH. Then, from known heats of formation $\Delta H_f^0(6) \leq x + 74.6 \pm 1$ kcal/mol, $\Delta H_f^0(7) \leq x + 103.5 \pm 0.1$ kcal/mol, and $\Delta H_f^0(7) - \Delta H_f^0(6) \geq 28.9 \pm 1$ kcal/mol. This is the difference between the $\beta$ (C–H) bond energy in ethanol and the C–Br bond energy in bromoethanol.

To pursue this matter further, we would need to know the C–Br bond energy in bromoethanol. One might imagine a dissociative ionization experiment to arrive at this value by observing the A.P. of Br$^+$ from bromoethanol. Assuming a C–Br bond energy of \(-70\) kcal/mol, the appearance potential would be about 14.85 eV. However, the observed A.P. of the same fragments, but with reversed charge (i.e., C$_2$H$_5$OH$^+$/Br) was found to be 10.774 \pm 0.005 eV. The higher energy process, forming Br$^+$ + C$_2$H$_3$OII, would be distinctly less favored (according to Stevenson’s rule) and almost certainly suffer a delayed onset.

We may pose the problem as follows: what is the effect of $\beta$ substitution in C$_2$H$_5$Br on the C–Br bond energy? The currently available experimental information is summarized in Table III. While limited by uncertainties in $\Delta H_f^0(\text{C$_2$H$_5$Cl})$ and $\Delta H_f^0(\text{C$_2$H$_5$Br})$, these data appear consistent with a C–Br bond energy of \(-69\) kcal/mol, perhaps diminishing with $\beta$ substitution of Cl and Br.

Alternatively, one may inquire about the effect of $\beta$ substitution on the $\alpha$ (C–H) bond energy in ethane. The currently available information is summarized in Table IV. These data show a similar trend to the ones in Table III (to be expected for Cl and Br substitution, since the same heats of formation for C$_2$H$_4$Cl and C$_2$H$_4$Br were used in both tables), but with the additional information that substitution of the highly electronegative F appears to increase the $\alpha$ (C–H) bond energy. Hence, there may be a weak effect due to the electronegativity of the substituent. The electronegativity of OII is estimated to be close to that of Br, using Mulliken’s criterion that electronegativity is proportional to the sum of ionization potential and electron affinity.

If we compare the C–H and C–Br bond energies with corresponding $\beta$ substituents H, Cl, and Br, we find differences (in kcal/mol) of 30.2 \pm 0.2, 30.7 \pm 1, and 30.4 \pm 0.3 kcal/mol, nearly constant and slightly higher than the value ($\approx 28.9 \pm 1$) we had deduced as the difference between $\beta$ (C–H) bond energy in ethanol and the C–Br bond energy in bromoethanol.

Now we turn to an entirely different line of reasoning. Brehm et al.$^{12}$ display the onset of the second increase in $m/e=45$ from ethanol in greater detail than others, using photoelectron–photoion coincidence measurements. Their method rules out the possibility of autoionization as the cause of the second increase. We have attempted to read a threshold for this process from their Fig. 9 and obtain 11.9 \pm 0.1 eV. Their corresponding threshold for the initial onset of $m/e=45$ is read to be 10.73 \pm 0.02 eV and hence the difference is 1.17 \pm 0.1 eV=27 \pm 2 kcal/mol. We had previously deduced from our own data that the difference in energy between CH$_3$CHOH$^+$ and the C$_2$H$_5$O$^+$ isomer formed upon dissociative ionization of bromoethanol was \approx 173.9 kcal/mol.

### Table III: The effect of $\beta$ substitution on the C–Br bond energy (in kcal/mol, 0 K)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br–C$_2$H$_5$</td>
<td>69.3 \pm 0.5</td>
</tr>
<tr>
<td>Br–C$_2$H$_5$Cl</td>
<td>68.5 \pm 1.5</td>
</tr>
<tr>
<td>Br–C$_2$H$_5$Br</td>
<td>67.4 \pm 2.2</td>
</tr>
</tbody>
</table>

*From Ref. 40.

### Table IV: The effect of $\beta$ substitution on $\alpha$(C–H) bond energy (in kcal/mol, 0 K) in ethane.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–C$_2$H$_5$</td>
<td>99.5 \pm 0.5</td>
</tr>
<tr>
<td>H–C$_2$H$_5$F</td>
<td>102.9 \pm 2.6</td>
</tr>
<tr>
<td>H–C$_2$H$_5$Cl</td>
<td>99.6 \pm 1.9</td>
</tr>
<tr>
<td>H–C$_2$H$_5$Br</td>
<td>97.8 \pm 2.4</td>
</tr>
</tbody>
</table>

*From Ref. 40. 

\[ \Delta H_f^0(\text{C$_2$H$_5$F}) \text{ and } \Delta H_f^0(\text{H}) \text{ from Ref. 3;} \text{ } \Delta H_f^0(\text{C$_2$H$_5$Cl}) = -10.65 \text{ kcal/mol from ab initio calculations of Chen, Rauk, and Tschuikow-Roux, J. Chem. Phys. 93, 6620 (1990).} \text{ } (H_{298}-H_0) \text{ C$_2$H$_5$F estimated from frequencies given by Shimanouchi (footnote b of Table III).} \text{ } (H_{298}-H_0) \text{ C$_2$H$_5$F is estimated to be 3.0 kcal/mol by comparison with corresponding quantities for C$_2$H$_5$, C$_2$H$_4$, and C$_2$H$_5$F. Chen et al. (above) calculate 3.16 kcal/mol for this quantity.} \text{ } \Delta H_f^0(\text{C$_2$H$_5$Cl}) \text{ and } \Delta H_f^0(\text{H}) \text{ from Ref. 3;} \text{ } \Delta H_f^0(\text{C$_2$H$_5$Cl}) \text{ and heat capacity corrections are the same as in footnote b of Table III.} \text{ } \Delta H_f^0(\text{C$_2$H$_5$Br}) \text{ and } \Delta H_f^0(\text{H}) \text{ from Ref. 3;} \text{ } \Delta H_f^0(\text{C$_2$H$_5$Br}) \text{ and heat capacity corrections are the same as in footnote c of Table III.} \]
and the C-Br bond energy in bromomethanol. The value of
reactions, then the difference between AHe(9) and AHe(8) is
the difference between the 0 (C-H) bond energy in ethanol
AHe(8) (10.774±0.005 eV) is independent of the value mea-
sured for reaction (4) and inferred for reaction (6) above. The
reliable is still D,(Br-CH,CH,)=69.3±0.5 kcaUmo1. If we take
energies deduced above (328.9± 1 kcal/mol), we arrive at a
photoelectron coincidence" and in a charge-transfer break-
has been observed in photoionization," photoion-
down diagram," the latter with sparse points. It has not been
D. Dynamics of dissociation of ethanol cation
In the dissociative ionization process
CD2CH2OH+ hν→(CD2CH2OH*)+D+ e,
the product ion displays a photoion yield curve which appears
to be identical, within experimental uncertainty, to the
m/e=45 ion from undeuterated ethanol, as well as to m/e
=48 from CD2CH2OH, but it is ~40 times weaker. We know
that this species must have the CH2CHOH+ structure near
threshold. Hence, although the reaction as written implies β
(C-H) bond cleavage, rearrangement and H/D scrambling
must occur at the dissociative ionization threshold (~10.8
eV). At about 11.9 eV, a further increase in the product ion
yield occurs, as with m/e=45 from undeuterated ethanol. It has
been observed in photoionization,10 photoion-
photoelectron coincidence12 and in a charge-transfer break-
down diagram,11 the latter with sparse points. It has not been
observed in a more recent photoion photoelectron coinci-
dence experiment,41 but very few points were measured in the
critical energy region.
We tentatively identify this second increase with forma-
tion of the cyclic protonated oxirane structure. We know that
it is formed in the dissociative ionization of bromomethanol
and its heat of formation matches the onset of the second
increase. Once formed, it does not rearrange spontaneously
to the ground state structure. If it did, the resulting internal
vibrational energy would result in dissociation and the sec-
ond increase would not be observable. Earlier studies34 sug-
gested the possibility of this rearrangement, but subsequent
experiments32 indicated that the oxirane structure was more
robust. The calculations of Nobes et al.15 indicate that there
is a barrier of ~32 kcal/mol for the rearrangement of cyclic
protonated oxirane to CH3CHOH+. According to their calcu-
lations, the transition state has the form

\[
\text{CH}_3\text{CHOH}^+ \rightarrow \text{CH}_2\text{CHOH}^+ \text{H}^+ e^-. \tag{9}
\]

which then reverts to the hydroxyethylene structure
CH2CHOH+. Their calculations are somewhat ambiguous
as to the stability of CH2CHOH+. At lower levels of calcu-
lation, there is a barrier to isomerization of CH2CHOH+
to the ground state structure, but this barrier disappears at
higher levels.

The photoion yield curve of CD2CH2OH+ (CD2CH2OH)
appearing in Fig. 7 bears on this question. This curve differs
from that of CH3CHOH+ (CH3CHOH) in Fig. 6 and from
CH3CHOH+ (CH3CHOH) in Fig. 5 and hence must corre-
spond to photodissociation of a distinct species CD2CH2OH.
This ion is observed as an undissociated species at an onset
energy about 40 kcal/mol above that of the ground state
structure. Dissociation of the ground state structure com-
mences about 10 kcal/mol above its onset. Hence, if the cat-
ion formed upon ionization of CD2CH2OH were to convert
rapidly to the ground state structure, it would decompose.
The fact that it does not implies some stability in a potential
well for that cation.

The shape of the curve in Fig. 7 (gradually increasing
ion yield) can be interpreted as a transition between a neutral
and cation structure having substantially different geom-
eties. One possible inference is that CD2CH2OH and
CD2CH2OH+ differ in geometry and that CD2CH2OH+ has a

<table>
<thead>
<tr>
<th>Product radical</th>
<th>( \Delta H_{298}^0 ) (kcal/mol)</th>
<th>( D_{298}(R-H) ) (kcal/mol)</th>
<th>( \Delta H_{298}^o ) (kcal/mol)</th>
<th>( D_{298}(R-H) ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3CHOH</td>
<td>(-15.6(-13.7)^a)</td>
<td>(92.6(-94.5)^a)</td>
<td>(-12.4(-10.5)^a)</td>
<td>(91.1(-93)^a)</td>
</tr>
<tr>
<td>CH3CH2OH</td>
<td>(-8.7(2)^a)</td>
<td>(99.5(2)^a)</td>
<td>(-5.5(2)^a)</td>
<td>(98(2)^a)</td>
</tr>
<tr>
<td>C3H5O</td>
<td>(-3.7(2)^a)</td>
<td>(104.6(2)^a)</td>
<td>(-0.4(2)^a)</td>
<td>(103.1(2)^a)</td>
</tr>
</tbody>
</table>

\( ^a\)Present results
\( ^b\)Reference 1, given at 298 K. However, it may be 1-3 kcal/mol higher (see the text).
\( ^c\)Based on \( D_{298}(Br-CH2CH2OH)=69\pm2\) kcal/mol; see the text for details.
\( ^d\)Reference 4.
an apparently anomalous second increase has been reported in the photoion yield curve or breakdown diagram of m/e =45 ions from ethanol, which we tentatively ascribe to formation of protonated oxirane cation+H.

ACKNOWLEDGMENTS

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APPENDIX

1. Thermal broadening function appropriate to decomposition processes from ethanol

From the expression given by Haarhoff and the vibrational frequencies for ethanol given by Gurvich et al., one obtains

\[ I_{3/2} = \frac{\text{const}}{(1 + \epsilon)^3} \left( \frac{1 + \epsilon}{2} \right) \left( \frac{1 + \epsilon}{2} \right)^{2/3} \left( \frac{1}{1 + \epsilon} \right)^{1.086} \]

\[ I_{5/2} = \frac{\text{const}}{(1 + \epsilon)^5} \left( \frac{1 + \epsilon}{2} \right) \left( \frac{1 + \epsilon}{2} \right)^{2/5} \left( \frac{1}{1 + \epsilon} \right)^{0.918} \]

Here, \( I_{3/2} \) and \( I_{5/2} \) represent the state densities as a function of the energy of \( \text{C}_2\text{H}_5\text{OH} \) above its zero point energy \( \epsilon_z \), and \( \epsilon \) is expressed in units \( \epsilon_z \).

For subsequent manipulation, it is convenient to fit these expressions to a form \( n! e^{-n!} \), where \( n \) is an integer. For the examples above, we find

\[ I_{3/2} = \text{const} \ e^{-14.28} \]

\[ I_{5/2} = \text{const} \ e^{-18.52} \]

When these expressions are combined with the Boltzmann function, i.e., \( \rho e^{-\frac{I.P.}{kT}} \), with \( T = 298 \) K, we arrive at the thermal broadening functions, which have the same form for cases (1) and (2), i.e., \( \rho e^{-\frac{I.P.}{kT}} e^{-\frac{I.P.}{kT}} \), but with a fictitious \( T \), which is 403.94 K for case (1) and 387.06 K for case (2).

2. Thermal broadening function appropriate to decomposition processes from bromoethanol

Again using Haarhoff's equation and vibrational frequencies for bromoethanol given by Thomassen et al., one obtains

\[ I_{3/2} = \text{const} \ e^{-18.52} \]

\[ I_{5/2} = \text{const} \ e^{-22.5} \]

When these expressions are combined with the Boltzmann function, i.e., \( \rho e^{-\frac{I.P.}{kT}} \), with \( T = 298 \) K, we arrive at the thermal broadening functions, which have the same form for cases (1) and (2), i.e., \( \rho e^{-\frac{I.P.}{kT}} e^{-\frac{I.P.}{kT}} \), but with a fictitious \( T \), which is 403.94 K for case (1) and 387.06 K for case (2).
\[
I_{3/2} = \frac{\text{const}}{(1 + \epsilon)} \left[ \frac{1 + \epsilon}{2} \left( \frac{1}{1 + \frac{2}{\epsilon}} \right)^{22.5} \right] \times \left[ 1 - \frac{1}{(1 + \epsilon)^2} \right]^{1.415 \times 967.8}
\]

and

\[
I_{5/2} = \frac{\text{const}}{(1 + \epsilon)} \left[ \frac{1 + \epsilon}{2} \left( \frac{1}{1 + \frac{2}{\epsilon}} \right)^{21.5} \right] \times \left[ 1 - \frac{1}{(1 + \epsilon)^2} \right]^{1.219 \times 921.4}
\]

Proceeding as in Sec. 1 of the Appendix, above, these functions are numerically approximated by

- case (1) \(I_{3/2}=\text{const} \epsilon^2 e^{-0.404 \cdot 796(\epsilon)}\)
- case (2) \(I_{5/2}=\text{const} \epsilon^2 e^{-20.903 \cdot 87(\epsilon)}\)

After combining these expressions with the Boltzmann factor \(T=298\, \text{K}\), we arrive at the same broadening function as for ethanol \(\rho e^{-E/kT} \propto E^2 e^{-E/kT}\), but with different fictitious temperatures \(T=443.07\, \text{K}\) for case (1) and \(419.06\, \text{K}\) for case (2).