

The heats of formation of some $C_2H_5O^+$ isomers, relevant bond energies in ethanol and PA(CH₃CHO)

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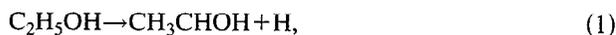
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The ionization potentials of the transient species CH_3CH_2O , CH_3CHOH , and CH_2CH_2OH (generated by the F+ethanol reactions) are measured by photoionization mass spectrometry: I.P.(CD_3CD_2O)= 10.29 ± 0.08 eV (tentative), I.P.(CH_3CHOH) < 6.85 eV, and I.P.(CD_2CH_2OH) $\leq 8.35\pm 0.06$ 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 CH_3CHOH^+ from ethanol enables one to infer the proton affinity of acetaldehyde to be $\geq 183.8\pm 0.2$ 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 $C_2H_5O^+$ isomer having the oxirane structure, with $\Delta H_{f_0}^0$ 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



Alfassi and Golden¹ obtained $D_{298} = 93.0\pm 1.0$ kcal/mol for reaction (1); this value has been maintained in a 1982 review² and in a 1988 compilation.³ It corresponds to $\Delta H_{f_{298}}^0(CH_3CHOH) = -15.2\pm 1.0$ kcal/mol.² For reaction (3), Ervin *et al.*⁴ obtained $D_0 = 103.1\pm 0.9$ kcal/mol ($D_{298} = 104.6\pm 0.8$) kcal/mol, which corresponds to $\Delta H_{f_0}^0(CH_3CH_2O) = -0.4\pm 0.9$ kcal/mol [$\Delta H_{f_{298}}^0(CH_3CH_2O) = -3.7\pm 0.8$ kcal/mol] by combining a measured gas phase acidity with a measured electron affinity of CH_3CH_2O . To our knowledge, the dissociation energy of reaction (2) is not known. Hints *et al.*⁵ and Sapers and Hess⁶ studied the 193 nm laser photodissociation of chloro-, bromo-, and iodoethanol, which generate CH_2CH_2OH with various internal energies, but the bond energy, and hence $\Delta H_{f_0}^0(CH_2CH_2OH)$, could not be determined in these experiments. Tully⁷ has demonstrated the importance of CH_2CH_2OH in combustion and atmospheric chemistry as the initial product in the reaction of OH with C_2H_4 .

The heats of formation of the radical cations of these species are also of interest. An accurate heat of formation of CH_3CHOH^+ 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 CH_3CHOH^+ 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 measure-

ments 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 $CH_3CH_2O^+$ 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 CH_3O^+ from dissociative ionization of methanol, where the lower energy CH_2OH^+ fragment dominates. However, it is possible to deduce the heat of formation of $CH_3CH_2O^+$ if one can measure the ionization potential of CH_3CH_2O .

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 C_2D_5OH . They concluded that about 50% of H(D) abstraction resulted in formation of the ethoxy radical, with the remainder roughly split between CH_2CH_2OH and CH_3CHOH (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 $CH_2CH_2OH^+$ 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 photodissociative ionization of $BrCH_2CH_2OH$, which presumably would form

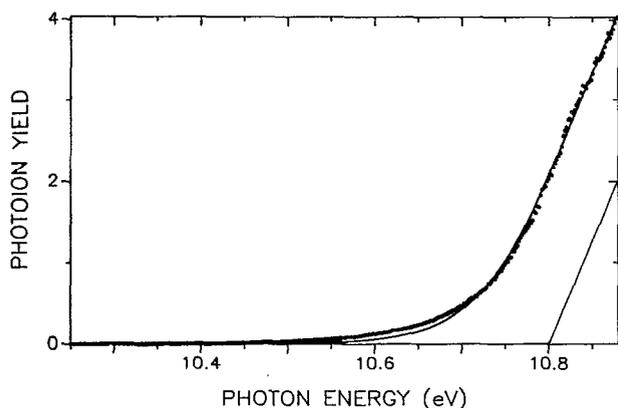


FIG. 1. The photoion yield curve of $m/e=45$ ion from ethanol. The smooth curve drawn is the best fit of a linear kernel function convoluted with a thermal broadening function (see the text). The sloped line is the kernel function, displaced to its hypothetical position at 0 K.

$CH_2CH_2OH^+ + Br$. These proposed experiments and their results are discussed below.

II. EXPERIMENTAL ARRANGEMENT

The transient species CD_3CD_2O , CH_3CHOH , and CD_2CH_2OH were prepared *in situ* by reaction of F atoms with CD_3CD_2OH , ordinary ethanol, and CD_3CH_2OH , 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.¹⁴ CD_3CH_2OH , CH_3CH_2OD , and bromoethanol were obtained from Aldrich Chemical Company, while CD_3CD_2OH was from Cambridge Isotope Laboratories. The isotopic purity, as stated by the manufacturer, was 99.5 at.% D for CH_3CH_2OD , 99 at.% D for CD_3CH_2OH , and 98 at.% D for CD_3CD_2OH .

III. EXPERIMENTAL RESULTS

A. The heat of formation of CH_3CHOH^+

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_3CHOH^+ because it is the lowest energy isomer¹⁵ and its formation from $CH_3CH_2OH^+$ 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 $\Delta H_f^0(CH_3CHOH^+)$, 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's¹⁶ expression for the rovibrational state density ρ . 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.*¹⁷ 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 $\phi(E-E_t)=c(E-E_t)$ and an exponential function $\phi(E-E_t)=c[1-e^{-b(E-E_t)}]$, where E_t 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 $\Delta H_f^0(C_2H_5OH) = -51.88 \pm 0.03$ kcal/mol (Ref. 17), and $\Delta H_f^0(H) = 51.633$ kcal/mol, this threshold yields $\Delta H_f^0(CH_3CHOH^+) \leq 145.6 \pm 0.1$ kcal/mol.

For purposes of comparison, the 0 K threshold given by Refaey and Chupka¹⁰ was 10.78 ± 0.02 eV. Brehm *et al.*¹² 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 $CH_2CH_2OH^+$

Our initial attempt to determine the heat of formation of this isomeric form utilized CD_3CH_2OH as the precursor. The expectation was that the photoion yield curve of $CD_2CH_2OH^+$ would differ from that of CD_3CHOH^+ , and that the threshold for the former would provide a basis for arriving at $\Delta H_f^0(CH_2CH_2OH^+)$.

The result was that the photoion yield curve of $m/e=47$ (nominally $CD_2CH_2OH^+$) was essentially the same as $m/e=48$ (CD_3CHOH^+), 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^{18,19} used isotope labeling to examine the decomposition of $(C_2H_5O)^+$ to both $(H_3O)^+$ and $C_2H_3^+$. 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.”¹⁹ We infer that the same behavior occurs for $C_2H_6O^+$ ions decomposing to $C_2H_5O^+$ fragments. The large isotope effect observed here is similar to that postulated by Keyes and Harrison¹⁹ ($k_H/k_D=1.30$) favoring transfer of H from carbon to oxygen in the reaction



The second attempt to determine $\Delta H_f^0(CH_2CH_2OH^+)$ was based on bromoethanol ($BrCH_2CH_2OH$) as a precursor.

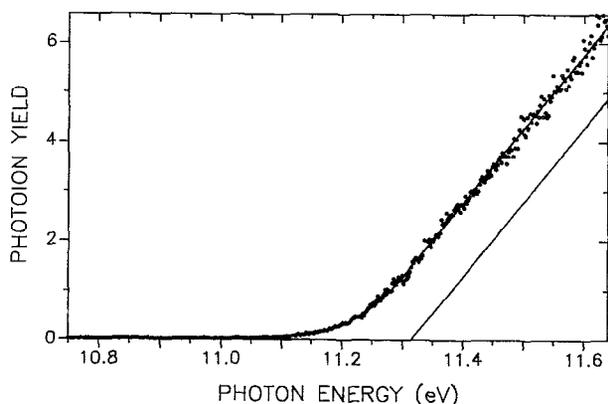


FIG. 2. The photoion yield curve of CH_2OH^+ from bromoethanol. The smooth curve drawn through the data points is the best fit of a linear kernel function convoluted with a thermal broadening function appropriate for bromoethanol. The sloping line is the kernel function, displaced to its hypothetical position at 0 K.

Since C–Br bonds are typically ~ 30 kcal/mol weaker than C–H bonds, it was anticipated that the first fragment following photoionization of bromoethanol would be $CH_2CH_2OH^+$ (+Br). If the heat of formation of bromoethanol were well established, the threshold for this photodissociative ionization process could conceivably lead to $\Delta H_f^0(CH_2CH_2OH^+)$. Unfortunately, $\Delta H_f^0(BrCH_2CH_2OH)$ 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



One of the products CH_2OH^+ has a well-established heat of formation 171.6 ± 0.2 kcal/mol (Ref. 20) at 0 K. The value of $\Delta H_f^0(CH_2Br)$ is less certain. Tschuikow-Roux and collaborators^{21,22} have arrived at $\Delta H_{f_{298}}^0(CH_2Br) = 40.4 \pm 1.0$ kcal/mol based on an analysis of thermochemical and kinetic data. If we accept this result, it is equivalent to $\Delta H_f^0(CH_2Br) = 42.9 \pm 1.0$ kcal/mol.

1. A.P.($CH_2OH^+/BrCH_2CH_2OH$) and $\Delta H_f^0(BrCH_2CH_2OH)$

The photoion yield curve of CH_2OH^+ 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 inter-

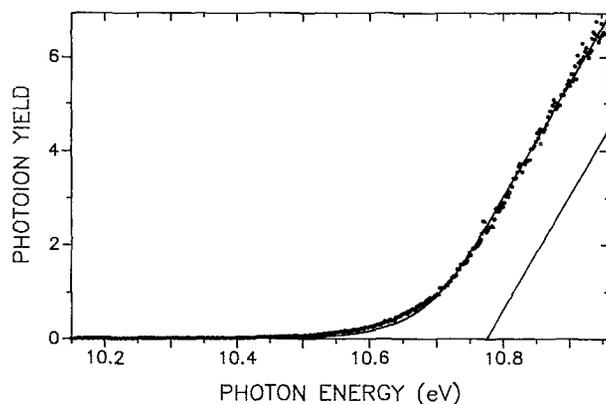


FIG. 3. The photoion yield curve of $m/e=45$ ion from bromoethanol. The smooth curve is the best fit of a linear kernel function convoluted with the same thermal broadening function used in Fig. 2. The sloping line is again the hypothetical 0 K fragmentation function.

nal energy of 0.099 eV at 298 K. The vibrational frequencies of bromoethanol were taken from Thomassen *et al.*²³ From this threshold, and the aforementioned $\Delta H_f^0(CH_2OH^+)$ and $\Delta H_f^0(CH_2Br)$, one can compute $\Delta H_f^0(BrCH_2CH_2OH) \geq -46.4 \pm 1$ kcal/mol.

2. A.P.[($CH_2CH_2OH^+$)?/ $BrCH_2CH_2OH$] and $\Delta H_f^0[(CH_2CH_2OH^+)?]$

The photoion yield curve of $m/e=45$ 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.

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



By combining this threshold with $\Delta H_f^0(Br) = 28.18$ kcal/mol (Ref. 17) and $\Delta H_f^0(BrCH_2CH_2OH)$ obtained in Sec. II B 1, we deduce $\Delta H_f^0[(CH_2CH_2OH^+)?] \approx 173.9$ kcal/mol. In principle, the thresholds for reactions (4) and (5) are both upper limits. In the evaluation of $\Delta H_f^0[(CH_2CH_2OH^+)?]$, 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 $\Delta H_f^0(CH_2Br)$ must be retained, and hence the result must remain approximate.

C. The transient species C_2H_5O , CH_3CHOH , and CH_2CH_2OH

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

1. Photoion yield curve of C_2H_5O

Initially, the reaction of F atoms with C_2H_5OD was employed. According to Bogan and Nesbitt,¹³ about 50% of the hydrogen abstraction reactions should yield C_2H_5O , with the remaining 50% shared between CH_2CH_2OD and CH_3CHOD . The latter would appear at $m/e=46$ upon photoionization, whereas the desired C_2H_5O 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 $1329 \pm 2 \text{ \AA} = 9.33 \pm 0.01 \text{ eV}$. To check on this observation, F atoms were reacted with C_2D_5OH , and the photoion yield curve of $m/e=50$ ($C_2D_5O^+$) was examined. The resulting spectrum (*vide infra*) was quite different. There was no sign of a threshold at $\sim 1329 \text{ \AA}$. Consequently, another interpretation for Fig. 4(a) was sought.

Phenomenologically, Fig. 4(a) involves a loss of 2 amu from the precursor C_2H_5OD , 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 PH_3 ,²⁴ SiH_2 from SiH_4 ,²⁵ and Si_2H_4 and even Si_2H_2 from Si_2H_6 .²⁶ Loss of two H atoms from C_2H_5OD could generate $CH_2=CHOD$ (vinyl alcohol) or CH_3CDO (acetaldehyde). The adiabatic ionization potential of $CH_2=CHOH$ (*syn*) has been determined to be $9.30 \pm 0.05 \text{ eV}$,²⁷ whereas that of acetaldehyde is $10.2291 \pm 0.0007 \text{ eV}$.²⁸ 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 (C_2H_5OH) 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 ($9.33 \pm 0.01 \text{ eV}$) is within the error bounds found for vinyl alcohol by photoelectron spectroscopy ($9.30 \pm 0.05 \text{ eV}$) and the steps in the photoion yield curve occur at intervals of $1400 \pm 50 \text{ cm}^{-1}$, matching the vibrational frequency of $CH_2=CHOH^+$ observed in the photoelectron spectrum.²⁷ This ionization potential is significantly higher than the value (9.14 eV) initially reported by electron impact spectroscopy,²⁹ but closer to subsequent electron impact values $9.22 \pm 0.03 \text{ eV}$ (Ref. 30) and $9.26 \pm 0.1 \text{ eV}$.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 C_2D_5OH was then chosen as reactant. Here, $C_2D_5O^+$ from C_2D_5O will appear at $m/e=50$, while CD_3CDOH , CD_2CD_2OH , vinyl alcohol, and acetaldehyde will appear at lower masses. However, the bulk of the C_2D_5OH , which remains unreacted, can generate a background at $m/e=50$ in two ways:

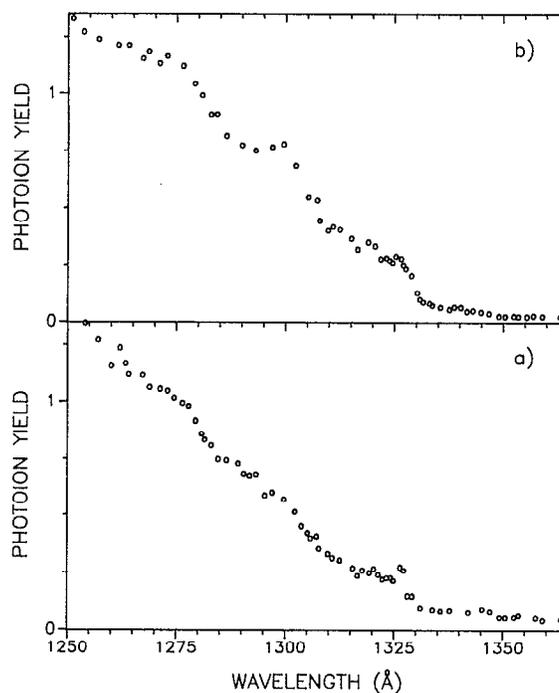


FIG. 4. (a) The photoion yield curve of $m/e=45$ obtained during the reaction of F atoms with C_2H_5OD . This curve could represent ionization of C_2H_5O , CH_3CDO , or $CH_2=CHOD$. (b) The photoion yield curve of $m/e=44$ obtained during the reaction of F atoms with C_2H_5OH . It represents the loss of two H atoms from C_2H_5OH and hence could refer to CH_3CHO or $CH_2=CHOH$. A comparison with the known I.P. of $CH_2=CHOH$ and the vibrational spacing in the cation (Ref. 27) proves that this is the photoion yield curve of $CH_2=CHOH$, vinyl alcohol. The almost identical appearance of (a) and (b) proves that (a) represents the photoion yield of $CH_2=CHOD$.

(1) mass leakage from parent ionization ($\sim 0.5\%$ of parent ion intensity);

(2) an isotopic impurity in the sample (CD_3CHDOH and CHD_2CD_2OH).

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 $\sim 1150 \text{ \AA}$ (10.78 eV) and a shallower slope toward longer wavelength, with an onset at $\sim 1205 \pm 10 \text{ \AA}$ ($10.29 \pm 0.08 \text{ eV}$), 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 CD_3CD_2OH should be CD_3CDOH^+ , appearing at a lower ($m/e=49$) mass than that represented by Fig. 5.

Bogan and Nesbitt¹³ also examined the $F+C_2D_5OH$ reaction, but with electron impact ionization. They observed an increase in the $m/e=50$ ion peak of $\sim 15\%$ – 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

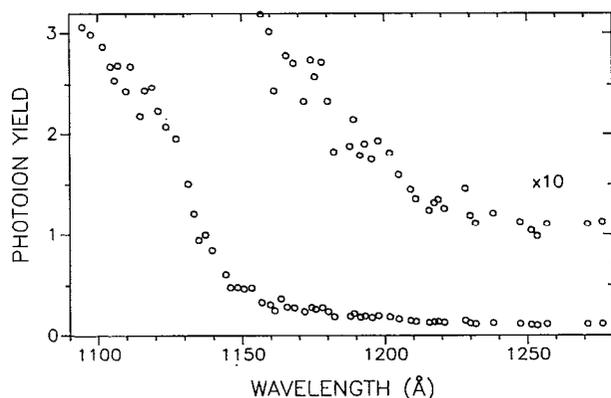


FIG. 5. The photoion yield curve of $CD_3CD_2O^+$ from CD_3CD_2O . The transient species was generated *in situ* by the reaction of F atoms with CD_3CD_2OH . The curve represents the net yield at $m/e=50$ (during and before abstraction) discussed in the text.

eV photons. Interestingly, they found that their detection sensitivity for C_2D_5O , relative to C_2D_5OH , decreased from 70 eV to a minimum at ~ 12 eV, and then increased again to 9 eV. However, at energies below the I.P. of C_2D_5OH (~ 10.47 eV), this ratio should become infinite and is not meaningful. They did not attempt to infer an ionization potential for C_2D_5O .

If we assume that the photoion yield curve of Fig. 5 is to be attributable entirely to the process $C_2D_5O + h\nu \rightarrow C_2D_5O^+$, then we are forced to conclude that adiabatic ionization at 10.29 eV is a weak process, and a much stronger one begins at ~ 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 $\Delta H_{f_0}^0(C_2D_5O) = -0.4 \pm 0.9$ kcal/mol (Ref. 4), implies $\Delta H_{f_0}^0(C_2H_5O^+) \approx 237$ kcal/mol.

2. Photoion yield curve of CH_3CHOH

We can estimate the adiabatic I.P. of CH_3CHOH as the difference between $\Delta H_{f_0}^0(CH_3CHOH^+)$, given in Sec. III A as $\leq 145.6 \pm 0.1$ kcal/mol, and $\Delta H_{f_0}^0(CH_3CHOH)$. To obtain the latter quantity, we correct $\Delta H_{f_{298}}^0(CH_3CHOH) = -15.2 \pm 1.0$ kcal/mol by choosing $(H_{298} - H_0)$ CH_3CHOH midway between that of CH_3CHO and CH_3CH_2OH , which gives $\Delta H_{f_0}^0(CH_3CHOH) = -12.0 \pm 1.0$ kcal/mol. The resulting predicted I.P. is ~ 6.83 eV. This is considerably lower than the I.P. (C_2H_5O) given above, and as we shall see, also lower than I.P. (CH_2CH_2OH). Hence, the reaction of ordinary, protonated ethanol with F atoms, which will generate all three isomers, provides a low energy window at $m/e=45$, where only ionization of CH_3CHOH should be occurring.

The photoion yield curve of $m/e=45$ consequent upon this abstraction reaction, above 1600 Å, is seen in Fig. 6. The onset of ionization is gradual, from ~ 1800 to ~ 1660 Å, at which point there may be a weak autoionization or the beginning of a plateau region. The weak signal for this species is attributable to a lower production rate of the neutral, com-

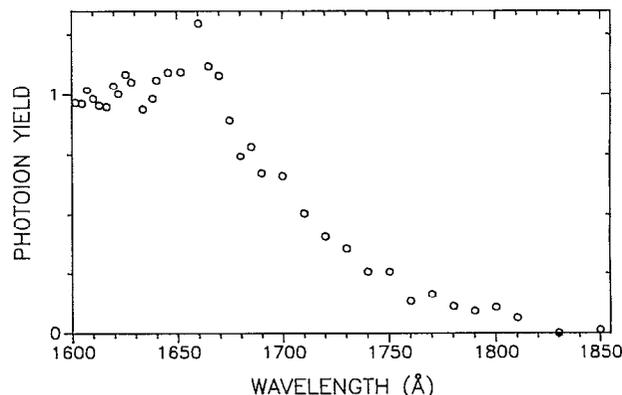


FIG. 6. The photoion yield curve of CH_3CHOH^+ from CH_3CHOH . The transient species was generated *in situ* by the reaction of F atoms with ordinary ethanol.

pared with relatively weak light emission from the hydrogen lamp. The choice of an onset is further hindered by the gradual decline of the ion yield curve as it approaches threshold. The first data point distinctly above the background level occurs at $1810 \text{ \AA} = 6.85$ eV; the next data point, at $1830 \text{ \AA} = 6.78$ eV, appears to be at the background level. The indication is that there is a substantial structural change accompanying ionization of CH_3CHOH , making a determination of the true adiabatic I.P. difficult.

3. Photoion yield curve of CH_2CH_2OH

In order to selectively photoionize this isomer, CD_3CH_2OH is chosen as reactant. The desired species CD_2CH_2OH should generate $m/e=47$ upon ionization, whereas CD_3CHOH and CD_3CH_2O should occur at $m/e=48$ and vinyl alcohol ($CD_2=CHOH$) at $m/e=46$. However, acetaldehyde (CD_3CHO) may also appear at $m/e=47$.

The photoion yield curve of $m/e=47$ ions observed during the fluorine atom abstraction reactions with CD_3CH_2OH is shown in Fig. 7. One sees a dramatic increase in the ion yield curve at $\sim 1210 \text{ \AA}$, 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 ~ 1350 – $1485 \pm 10 \text{ \AA}$, and further tailing to $\sim 1515 \pm 15 \text{ \AA}$, and perhaps lower. Thus, the adiabatic I.P. of CD_2CH_2OH is $\leq 8.35 \pm 0.06$ eV, and perhaps $\leq 8.18 \pm 0.08$ 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. (CD_2CH_2OH) with estimates based on our measured $\Delta H_{f_0}^0[(CH_2CH_2OH^+)] \approx 173.9$ kcal/mol obtained in Sec. III B 2. We consider first the case of bromoethanol. The C–Br bond energy in CH_3Br and C_2H_5Br is 69.5 ± 0.3 and 69.3 ± 0.5 kcal/mol at 0 K. If we transfer such a bond energy to $BrCH_2CH_2OH$, we deduce $\Delta H_{f_0}^0(CH_2CH_2OH) = -5.5 \pm 2$ kcal/mol and hence I.P. (CH_2CH_2OH) would be

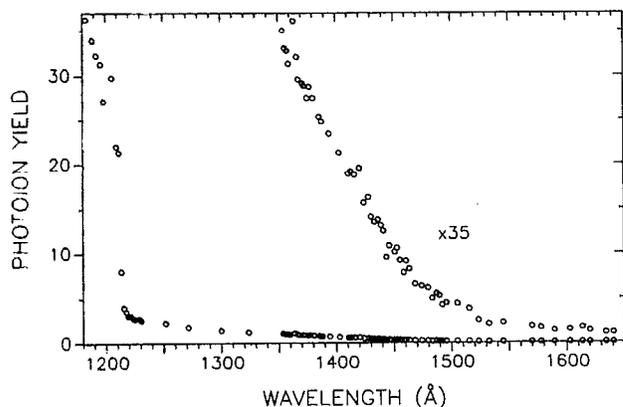


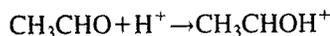
FIG. 7. The photoion yield curve of $m/e=47$ ions observed during the fluorine atom abstraction reactions with $\text{CD}_3\text{CH}_2\text{OH}$. The abrupt increase in ion yield at ~ 1210 Å is attributed to the presence of acetaldehyde CD_3CHO . Above 1220 Å, the neutral species studied is almost certainly $\text{CD}_2\text{CH}_2\text{OH}$, but the structure of the cation formed requires discussion (see the text).

estimated to be 7.78 ± 0.1 eV. Alternatively, if we transfer the C–H bond energy from ethane to $\text{H}-\text{CH}_2\text{CH}_2\text{OH}$ in ethanol, we infer an I.P. ($\text{CH}_2\text{CH}_2\text{OH}$) of ~ 7.7 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.

IV. INTERPRETATION OF RESULTS

A. The proton affinity of acetaldehyde

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



at 298 K. We have determined $\Delta H_{f_0}^0(\text{CH}_3\text{CHOH}^+) \leq 145.6 \pm 0.1$ kcal/mol. To correct this quantity to 298 K, we once again assume that $(H_{298} - H_0)$ CH_3CHOH^+ lies midway between that of CH_3CHO and $\text{CH}_3\text{CH}_2\text{OH}$. This adjustment results in $\Delta H_{f_{298}}^0(\text{CH}_3\text{CHOH}^+) \leq 142.3 \pm 0.2$ kcal/mol. The quantities $\Delta H_{f_{298}}^0(\text{CH}_3\text{CHO}) = -39.6 \pm 0.1$ kcal/mol and $\Delta H_{f_{298}}^0(\text{H}^+) = 365.7$ kcal/mol are firm literature values.³ Therefore, $\text{P.A.}(\text{CH}_3\text{CHO}) \geq 183.8 \pm 0.2$ 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.

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

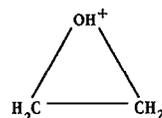
Process	Threshold
$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHOH}^+ + \text{H} + e$	10.801 ± 0.005
$\text{BrCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH}^+ + \text{CH}_2\text{Br} + e$	11.314 ± 0.005
$\text{BrCH}_2\text{CH}_2\text{OH} \rightarrow [(\text{CH}_2\text{CH}_2\text{OH}^+)] + \text{Br} + e$	10.774 ± 0.005
$\text{CH}_3\text{CH}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{O}^+ + e$	10.29 ± 0.08^a
$\text{CH}_3\text{CHOH} \rightarrow \text{CH}_3\text{CHOH}^+ + e$	< 6.85
$\text{CD}_2\text{CH}_2\text{OH} \rightarrow (\text{CD}_2\text{CH}_2\text{OH}^+)? + e$	$\leq 8.35 \pm 0.06$
	$\leq 8.18 \pm 0.08^a$

^aTentative.

Smith and Radom⁸ have recently calculated $\text{P.A.}(\text{CH}_3\text{CHO}) = 184.1$ 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)] based on proton transfer equilibria and proton transfer reactions. The present result is seen to be in excellent agreement with the calculated value.

B. The heats of formation and structures of C₂H₅O⁺ isomers

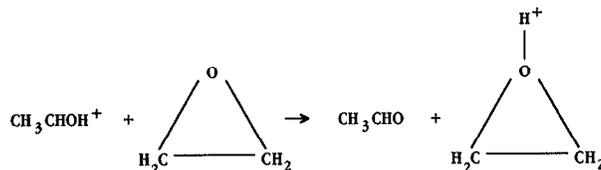
In an earlier calculation from Radom's laboratory, by Nobes *et al.*,¹⁵ the relative energies and structures of 16 possible $\text{C}_2\text{H}_5\text{O}^+$ isomers were calculated at the third-order Møller–Plesset (MP3)/6-31G** level. The lowest energy (most stable) isomer was, as expected, CH_3CHOH^+ . The next most stable $\text{H}_3\text{C}-\text{O}-\text{CH}_2^+$ is unlikely to be formed in the current experiments, but could be determined using dimethyl ether as a target.³² This is followed by $\text{CH}_2=\text{CH}-\text{OH}_2^+$, also unlikely to be generated in our experiments. The fourth and fifth isomers in order of stability were



29.4 kcal/mol above the most stable isomer, and $\text{CH}_2\text{CH}_2\text{OH}^+$, 51.4 kcal/mol above CH_3CHOH^+ .

The heat of formation of the species we have been labeling [$(\text{CH}_2\text{CH}_2\text{OH}^+)?$] is found to be $\sim 28.3 \pm 1$ kcal/mol above CH_3CHOH^+ . 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 $\text{CH}_2\text{CH}_2\text{OH}^+$. 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 $\text{C}_2\text{H}_5\text{O}^+$ is formed.

Solka and Russell³³ had come to this conclusion earlier in their study of electron impact ionization of bromoethanol. They inferred the heat of formation of the $m/e=45$ ion from bromoethanol to be 166 ± 1 kcal/mol, about 26 kcal/mol higher than their value for the ground state structure (CH_3CHOH^+). They were guided in their interpretation by a prior study performed by Beauchamp and Dunbar.³⁴ These latter authors studied the reaction



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 ± 4 kcal/mol. Although Solka and Russell obtained 10.47 ± 0.05 eV for their appearance potential of $m/e=45$ ion from bromoethanol (cf. 10.774 ± 0.005 eV in the present work), and the value of ΔH_f^0 (bromoethanol) used was not stated, their inference regarding the isomeric form of $\text{C}_2\text{H}_5\text{O}^+$ 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 $D_0(Br-CH_2CH_2OH)$ will be closed. The I.P.(CH_2CH_2OH) presumably refers to a linear structure, whereas the A.P.($CH_2CH_2OH^+/BrCH_2CH_2OH$) may refer to a cyclic structure. If we use our estimated $\Delta H_{f_0}^0(CH_2CH_2OH)$ and the measured I.P.(CH_2CH_2OH), we arrive at $\Delta H_{f_0}^0(CH_2CH_2OH^+)$, 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_2CH_2OH 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.*, $CH_2CH_2OH^+$ 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–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.*¹⁵ 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_3O^+ was found to be a metastable triplet, both by calculation³⁵ 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 Hamill³⁸ 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) 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 $(C_2H_5)_2O$ and C_2H_5OH . Their average value for $\Delta H_f^0(C_2H_5O^+)$ was 9.15 eV=211 kcal/mol (presumably re-

TABLE II. Heats of formation of some $C_2H_5O^+$ isomers (in kcal/mol at 0 K).

Species	Present results	<i>Ab initio</i> calculations	Other experimental values
CH_3CHOH^+	$\leq 145.6 \pm 0.1$	145.5 ^a 144.1 ^d	$146 \pm 3^b, 142^c$
$\begin{array}{c} \text{OH} \\ / \quad \backslash \\ \text{H}_2\text{C} \quad \text{CH}_2 \end{array}$	$(\approx 173.9)^e$	174.9 ^f 171.9 ^d	172 ± 3^b 168 ^c
$CH_2CH_2OH^+$	$\leq 187 \pm 2^g$	196.8 ^f Unstable ^d	192(estimated) ^h
$CH_3CH_2O^+$	$\sim 237^i$	Unstable ^j 238.1 ^d	214 ^k

^aFrom Ref. 8 either using G2 energies directly, or from their P.A. (CH_3CHO). To arrive at $\Delta H_{f_0}^0(CH_3CHOH^+)$, we use $\Delta H_f^0(CH_3CHO) = -37.0 \pm 0.1$ kcal/mol and $\Delta H_f^0(H^+) = 365.2$ kcal/mol from Ref. 3.

^bFrom Refs. 34 and 42 corrected to 0 K.

^cFrom Ref. 3 corrected to 0 K.

^dFrom Ref. 37

^eFrom A.P.($C_2H_5O^+$ /bromoethanol), after initially determining $\Delta H_f^0(BrCH_2CH_2OH) \geq -46.4 \pm 1$ kcal/mol and assuming that the cyclic cation is formed.

^fFrom Ref. 15 and footnote a, above; it is not clear whether this is a minimum on the potential energy surface.

^gFrom I.P.(CH_2CH_2OH) $\leq 8.35 \pm 0.06$ eV and $D_0(H-CH_2CH_2OH) = 98 \pm 2$ kcal/mol.

^hR. D. Bowen, D. H. Williams, and G. Hvistendahl, *J. Am. Chem. Soc.* **99**, 7509 (1977).

ⁱFrom $\Delta H_f^0(C_2H_5O)$ given by Ervin *et al.* (Ref. 4) and I.P.(CH_3CH_2O)=10.29 \pm 0.08 eV, the current tentative result.

^jNobes *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.

^kReference 38, corrected to 0 K. Note that this result is based on a very questionable interpretation of data.

ferring to 298 K) and hence $\Delta H_{f_0}^0(C_2H_5O^+) \sim 214$ kcal/mol. Our current value is $\Delta H_{f_0}^0(C_2H_5O^+) \sim 237$ 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–H and O–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 [$D_0(CH_3CH_2O-H) = 103.1 \pm 0.9$ kcal/mol] is an acceptable alternative.

For the α (C–H) bond energy, we subtract I.P.(CH_3CHOH) < 6.85 eV from A.P.(CH_3CHOH^+/C_2H_5OH) = 10.801 ± 0.005 eV to yield $D_0(\alpha-CH) > 3.95$ eV = 91.1 kcal/mol. This apparently supports, but does not improve upon $D_0(\alpha-CH) = 91.5 \pm 1.0$ kcal/mol inferred from $D_{298} = 93.0 \pm 1.0$ kcal/mol given by Alfassi and Golden.¹ These latter authors measured an activation energy for the reaction $I + CH_3CH_2OH \rightarrow CH_3CHOH + HI$, and assumed a reverse activation energy of 1 ± 1 kcal/mol. In the late 1980's, Gutman and co-workers⁴⁰ were able to directly measure the activation energy for a number of $R + HI$ reactions

and concluded that they were negative and as low as -2 kcal/mol. If this correction is applicable to the HI+CH₃CHOH 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 $D_0(\alpha\text{-CH})=94.9$ kcal/mol. If we accept $1830 \text{ \AA}=6.78 \text{ eV}$ in Fig. 6 as the adiabatic I.P. of CH₃CHOH, then our experimental $D_0(\alpha\text{-CH})$ becomes 92.8 kcal/mol, which is just about within the uncertainty of the *ab initio* calculation.

To arrive at the β (C–H) bond energy, we have devised two independent arguments. It will be recalled that $\Delta H_{f_0}^0(\text{BrCH}_2\text{CH}_2\text{OH})$ was deduced to be $\geq -46.4 \pm 1$ kcal/mol from the A.P.(CH₂OH⁺/BrCH₂CH₂OH). Now consider the dissociation reactions



and



Let x be the heat of formation of CH₂CH₂OH. Then, from known heats of formation $\Delta H_0(6) \leq x + 74.6 \pm 1$ kcal/mol, $\Delta H_0(7) = x + 103.5 \pm 0.1$ kcal/mol, and $\Delta H_0(7) - \Delta H_0(6) \geq 28.9 \pm 1$ kcal/mol. This is the difference between the β (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., C₂H₄OH⁺+Br) was found to be 10.774 ± 0.005 eV. The higher energy process, forming Br⁺+C₂H₄OH, 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 β substitution in C₂H₅Br on the C–Br bond energy? The currently available experimental information is summarized in Table III. While limited by uncertainties in $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_4\text{Cl})$ and $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_4\text{Br})$, these data appear consistent with a C–Br bond energy of ~ 69 kcal/mol, perhaps diminishing with β substitution of Cl and Br.

Alternatively, one may inquire about the effect of β substitution on the α (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 C₂H₄Cl and C₂H₄Br were used in both tables), but with the additional information that substitution of the highly electronegative F appears to *increase* the α (C–H) bond energy. Hence, there may be a weak effect due to the electronegativity of the substituent. The electronegativity of OH 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 β substituents H, Cl, and Br, we find differences (in kcal/mol) of 30.2 ± 0.2 , 30.7 ± 1 , and 30.4 ± 0.3

TABLE III. The effect of β substitution on the C–Br bond energy (in kcal/mol, 0 K).

Bond	Energy
Br–C ₂ H ₅	69.3 ± 0.5^a
Br–C ₂ H ₄ Cl	68.5 ± 1.5^b
Br–C ₂ H ₄ Br	67.4 ± 2^c

^a $\Delta H_{f_0}^0(\text{C}_2\text{H}_5\text{Br})$ and $\Delta H_{f_0}^0(\text{Br})$ from Ref. 3; $\Delta H_{f_0}^0(\text{C}_2\text{H}_5)$ from Ref. 40.

^b $\Delta H_{f_{298}}^0(\text{BrC}_2\text{H}_4\text{Cl})$ and $\Delta H_{f_0}^0(\text{Br})$ from Ref. 3; $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_4\text{Cl}) = 21.8 \pm 1$ kcal/mol from Miyokawa and Tschuikow-Roux, J. Phys. Chem. **94**, 715 (1990). ($H_{298} - H_0$) for BrC₂H₄Cl was estimated to be 3.7 kcal/mol from frequencies given by Shimanouchi, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. 39, U.S. Government Printing Office (1972); ($H_{298} - H_0$) for C₂H₄Cl was estimated to be 3.2 kcal/mol by comparison of this quantity in C₂H₅, C₂H₆, and C₂H₅Cl. Chen and Tschuikow-Roux, J. Phys. Chem. **96**, 7266 (1992) obtain 3.42 kcal/mol for this latter quantity from an *ab initio* calculation.

^c $\Delta H_{f_{298}}^0(\text{BrC}_2\text{H}_4\text{Br})$ and $\Delta H_{f_0}^0(\text{Br})$ from Ref. 3; $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_4\text{Br}) = 32.3 \pm 2$ kcal/mol from Holmes and Lossing, J. Am. Chem. Soc. **110**, 7343 (1988). ($H_{298} - H_0$) for BrC₂H₄Br was estimated to be 3.8 kcal/mol from frequencies given by Shimanouchi (see footnote b above), while ($H_{298} - H_0$) for C₂H₄Br was estimated to be 3.2 kcal/mol in an analogous manner to obtaining this quantity for C₂H₄Cl (see footnote b above).

kcal/mol, nearly constant and slightly higher than the value ($\geq 28.9 \pm 1$) we had deduced as the difference between β (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 ± 0.1 eV. Their corresponding threshold for the initial onset of $m/e=45$ is read to be 10.73 ± 0.02 eV and hence the difference is $1.17 \pm 0.1 \text{ eV} = 27 \pm 2$ kcal/mol. We had previously deduced from our own data that the difference in energy between CH₃CHOH⁺ and the C₂H₅O⁺ isomer formed upon dissociative ionization of bromoethanol was ≈ 173.9

TABLE IV. The effect of β substitution on α (C–H) bond energy (in kcal/mol, 0 K) in ethane.

Bond	Energy
H–C ₂ H ₅	99.5 ± 0.5^a
H–C ₂ H ₄ F	102.9 ± 2^b
H–C ₂ H ₄ Cl	99.6 ± 1^c
H–C ₂ H ₄ Br	97.8 ± 2^d

^aFrom Ref. 40.

^b $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_5\text{F})$ and $\Delta H_{f_0}^0(\text{H})$ from Ref. 3; $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_4\text{F}) = -10.65$ kcal/mol from *ab initio* calculations of Chen, Rauk, and Tschuikow-Roux, J. Chem. Phys. **93**, 6620 (1990). ($H_{298} - H_0$) C₂H₅F estimated from frequencies given by Shimanouchi (footnote b of Table III). ($H_{298} - H_0$) C₂H₄F is estimated to be 3.0 kcal/mol by comparison with corresponding quantities for C₂H₅, C₂H₆, and C₂H₅F. Chen *et al.* (above) calculate 3.16 kcal/mol for this quantity.

^c $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_5\text{Cl})$ and $\Delta H_{f_0}^0(\text{H})$ from Ref. 3; $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_4\text{Cl})$ and heat capacity corrections are the same as in footnote b of Table III.

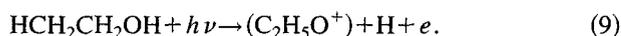
^d $\Delta H_{f_0}^0(\text{C}_2\text{H}_5\text{Br})$ and $\Delta H_{f_0}^0(\text{H})$ from Ref. 3; $\Delta H_{f_{298}}^0(\text{C}_2\text{H}_4\text{Br})$ and heat capacity corrections are the same as in footnote c of Table III.

TABLE V. The C–H and O–H bond energies in ethanol (kcal/mol) and the heats of formation of the corresponding radicals.

Product radical	$\Delta H_{f_{298}}^0$ (R)	$D_{298}(R-H)$	ΔH_f^0 (R)	$D_0(R-H)$
CH_3CHOH	$>-15.6(\sim-13.7)^a$ -15.2 ± 1.0^b	$>92.6(\sim94.5)^a$ 93.0 ± 1.0^b	$>-12.4(\sim-10.5)^a$ -12.0 ± 1.0^b	$>91.1(\sim93)^a$ 91.5 ± 1.0^b
CH_2CH_2OH	$(-8.7 \pm 2)^c$	$(99.5 \pm 2)^c$	$(-5.5 \pm 2)^c$	$(98 \pm 2)^2$
C_2H_5O	-3.7 ± 0.8^d	104.6 ± 0.8^d	-0.4 ± 0.9^d	103.1 ± 0.9^d

^aPresent results^bReference 1, given at 298 K. However, it may be 1–3 kcal/mol higher (see the text).^cBased on $D_0(Br-CH_2CH_2OH)=69 \pm 2$ kcal/mol; see the text for details.^dReference 4.

$-145.6 \approx 28.3$ kcal/mol. The near equality of these differences strongly suggests that the same isomeric species of $C_2H_5O^+$ is formed in both dissociations. Let us proceed on this assumption. Consider the two reactions

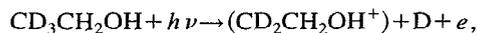


If the same isomeric form of $(C_2H_5O^+)$ is formed in both reactions, then the difference between $\Delta H_0(9)$ and $\Delta H_0(8)$ is the difference between the β (C–H) bond energy in ethanol and the C–Br bond energy in bromomethanol. The value of $\Delta H_0(8)$ (10.774 ± 0.005 eV) is independent of the value measured for reaction (4) and inferred for reaction (6) above. The value of $\Delta H_0(9)$ is obtained by correcting our reading of Brehm's data to 0 K, yielding 12.0 ± 0.1 eV. The difference between $\Delta H_0(9)$ and $\Delta H_0(8)$ is thus 1.226 ± 0.1 eV = 28.3 ± 2 kcal/mol, which is in good agreement with the first approach $\approx 28.9 \pm 1$ kcal/mol.

Of the C–Br bond energies listed in Table III, the most reliable is still $D_0(Br-C_2H_5)=69.3 \pm 0.5$ kcal/mol. If we take the C–Br bond energy in bromoethanol to be 69 ± 2 kcal/mol and combine it with the difference of C–H and C–Br bond energies deduced above ($\approx 28.9 \pm 1$ kcal/mol), we arrive at a β (C–H) bond energy in ethanol of 98 ± 2 kcal/mol. Table V summarizes the C–H and O–H bond energies for ethanol and the corresponding radical heats of formation.

D. Dynamics of dissociation of ethanol cation

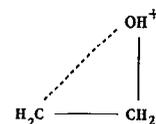
In the dissociative ionization process



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 CD_3CH_2OH , but it is ~ 40 times weaker. We know that this species must have the CH_3CHOH^+ 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 breakdown diagram,¹¹ the latter with sparse points. It has not been

observed in a more recent photoion-photoelectron coincidence experiment,⁴¹ but very few points were measured in the critical energy region.

We tentatively identify this second increase with formation of the cyclic protonated oxirane structure. We know that it is formed in the dissociative ionization of bromoethanol 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 second increase would not be observable. Earlier studies³⁴ suggested the possibility of this rearrangement, but subsequent experiments⁴² 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 CH_3CHOH^+ . According to their calculations, the transition state has the form



which then reverts to the hydroxyethylene structure $CH_2CH_2OH^+$. Their calculations are somewhat ambiguous as to the stability of $CH_2CH_2OH^+$. At lower levels of calculation, there is a barrier to isomerization of $CH_2CH_2OH^+$ to the ground state structure, but this barrier disappears at higher levels.

The photoion yield curve of $CD_2CH_2OH^+$ (CD_2CH_2OH) appearing in Fig. 7 bears on this question. This curve differs from that of CH_3CHOH^+ (CH_3CHOH) in Fig. 6 and from $CH_3CH_2O^+$ (CH_3CH_2O) in Fig. 5 and hence must correspond to photoionization of a distinct species CD_2CH_2OH . 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 commences about 10 kcal/mol above its onset. Hence, if the cation formed upon ionization of CD_2CH_2OH 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 geometries. One possible inference is that CD_2CH_2OH and $CD_2CH_2OH^+$ differ in geometry and that $CD_2CH_2OH^+$ has a

stable minimum. Another interpretation, perhaps more likely upon consideration of the *ab initio* calculations, is that CD₂CH₂OH⁺ is not stable and that the gradually increasing ion yield corresponds to formation of the protonated oxirane structure, which would manifest very slowly increasing Franck-Condon factors from threshold. This cation could survive intact until it acquired sufficient internal energy to overcome the barrier to dissociation. Recent, higher level calculations by Curtiss *et al.*³⁷ conclude that the CH₂CH₂OH⁺ structure does not represent a local minimum in the cation potential energy surface.

Some evidence for the formation of the oxirane structure, as well as CH₃CHOH⁺, can be found in the breakdown diagram of *n*-propanol and the photoion yield curve of *iso*-propanol presented in previous photoionization work,¹⁰ but additional studies would be required to substantiate these surmises.

V. CONCLUSIONS

(1) The appearance potential of CH₃CHOH⁺ from ethanol is found to be 10.801 ± 0.005 eV. This threshold implies Δ*H*_{f0}⁰(CH₃CHOH⁺) ≤ 145.6 ± 0.1 kcal/mol and a proton affinity of acetaldehyde of ≥ 183.8 ± 0.2 kcal/mol, in excellent agreement with the *ab initio* calculated value of Smith and Radom (184.1 kcal/mol), but about 2–3 kcal/mol lower than recently cited experimental values.

(2) The ionization potentials of CH₃CHOH and CH₃CH₂O are measured to be <6.85 and 10.29 ± 0.08 eV (tentative). The ionization potential of CD₂CH₂OH is found to be ≤ 8.35 ± 0.06 eV, perhaps ≤ 8.18 ± 0.08 eV, but the structure of the cation is probably not CD₂CH₂OH⁺, but rather the cyclic oxirane structure.

(3) Evidence is found for the formation of CH₂=CHOH (vinyl alcohol) and acetaldehyde in the F+ethanol reactions, presumably by successive abstraction. The adiabatic ionization potential of vinyl alcohol obtained by photoionization mass spectrometry is 9.33 ± 0.01 eV.

(4) The heat of formation of bromoethanol is found to be ≥ -46.4 ± 1 kcal/mol (0 K) and ≥ -52.2 ± 1 kcal/mol (298 K).

(5) Dissociative ionization of bromoethanol forms the protonated oxirane cation. Its heat of formation (0 K) is found to be ≈ 173.9 kcal/mol, about 28.3 kcal/mol above that of the ground state structure CH₃CHOH⁺.

(6) The heat of formation of CH₃CH₂O⁺, assumed to be a triplet, is deduced from Δ*H*_f⁰(CH₃CH₂O) and I.P.(CH₃CH₂O) to be ~237 kcal/mol, about 91 kcal/mol above the ground state structure.

(7) The α (C–H) bond energy in ethanol is found to be >91.1 kcal/mol (0 K), apparently supporting an earlier determination. However, both may be too low by 1–3 kcal/mol. The β (C–H) bond energy is inferred to be 98 ± 2 kcal/mol (0 K). The inference is based on a C–Br bond energy of 69 ± 2 kcal/mol in bromoethanol.

(8) The dynamics of dissociation of ethanol cations is discussed. Prior to the first dissociation (to CH₃CHOH⁺ + H), scrambling among H/D atoms attached to the carbon atoms occurs. About 27 ± 2 kcal/mol above the first fragmentation,

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.

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APPENDIX

1. Thermal broadening function appropriate to decomposition processes from ethanol

From the expression given by Haarhoff¹⁶ and the vibrational frequencies for ethanol given by Gurvich *et al.*,¹⁷ one obtains

case (1) 21 vibrations

$$I_{3/2} = \frac{\text{const}}{(1 + \epsilon)} \left[\left(1 + \frac{\epsilon}{2} \right) \left(1 + \frac{2}{\epsilon} \right)^{\epsilon/2} \right]^{22.5} \times \left[1 - \frac{1}{(1 + \epsilon)^2} \right]^{1.086 \ 232 \ 9}$$

and

case (2), 19 vibrations, two internal rotors

$$I_{5/2} = \frac{\text{const}}{(1 + \epsilon)} \left[\left(1 + \frac{\epsilon}{2} \right) \left(1 + \frac{2}{\epsilon} \right)^{\epsilon/2} \right]^{21.5} \times \left[1 - \frac{1}{(1 + \epsilon)^2} \right]^{0.918 \ 109 \ 6}$$

Here, *I*_{3/2} and *I*_{5/2} represent the state densities as a function of the energy of C₂H₅OH above its zero point energy ε_z, and ε is expressed in units ε_z.

For subsequent manipulation, it is convenient to fit these expressions to a form ρ ∝ ε^{*n*} e^{-*l*ε}, where *n* is an integer. For the examples above, we find

$$\text{case (1)} \ I_{3/2} = \text{const} \ \epsilon^{21.428 \ 36\epsilon}$$

and

$$\text{case (2)} \ I_{5/2} = \text{const} \ \epsilon^{18.539 \ 42\epsilon}$$

When these expressions are combined with the Boltzmann function, i.e., ρ e^{-*E*/*kT*}, with *T* = 298 K, we arrive at the thermal broadening functions, which have the same form for cases (1) and (2), i.e., ρ e^{-*E*/*kT*} ∝ E^{*n*} e^{-*E*/*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.*,²³ one obtains

case (1), 21 vibrations,

$$I_{3/2} = \frac{\text{const}}{(1+\epsilon)} \left[\left(1 + \frac{\epsilon}{2} \right) \left(1 + \frac{2}{\epsilon} \right)^{\epsilon/2} \right]^{22.5} \\ \times \left[1 - \frac{1}{(1+\epsilon)^2} \right]^{1.415\ 967\ 8}$$

and

case (2), 19 vibrations, two internal rotors,

$$I_{5/2} = \frac{\text{const}}{(1+\epsilon)} \left[\left(1 + \frac{\epsilon}{2} \right) \left(1 + \frac{2}{\epsilon} \right)^{\epsilon/2} \right]^{21.5} \\ \times \left[1 - \frac{1}{(1+\epsilon)^2} \right]^{1.219\ 921\ 4}$$

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

$$\text{case (1)} \quad I_{3/2} = \text{const} \epsilon^2 e^{24.040\ 296(\epsilon)}$$

and

$$\text{case (2)} \quad I_{5/2} = \text{const} \epsilon^2 e^{20.903\ 87(\epsilon)}$$

After combining these expressions with the Boltzmann factor ($T=298$ 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 $T=443.07$ K for case (1) and 419.06 K for case (2).

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