J. Phys. Chem. A **1997,** *101,* 373−376

Study of the CH_3CHOH Radical with Ultraviolet Photoelectron Spectroscopy[†]

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Received: May 7, 1996; In Final Form: July 8, 1996[⊗]

He I photoelectron spectra have been recorded for the $F + C_2H_5OH$ reaction, and a band has been identified associated with the primary reaction product CH_3CHOH. The first adiabatic and vertical ionization energies of this radical have been measured as (6.64 ± 0.03) and (7.29 ± 0.03) eV respectively. The assignment of this band to CH_3CHOH is supported by *ab initio* calculations performed at the G2 level of theory. Spectra recorded at different reaction times have demonstrated the short-lived nature of CH_3CHOH and the major pathway of the $F + C_2H_5OH$ reaction. The value measured for the adiabatic ionization energy has allowed the heat of formation of CH_3CHOH to be derived from the heat of formation of CH_3CHOH^+.

Introduction

The radicals obtained on loss of a hydrogen atom from ethanol are of considerable interest as they are oxidation intermediates in combustion processes. Alkoxy radicals and their isomers determine the initial products formed in the oxidation of hydrocarbons at temperatures below 500 K through reactions of the type $2RO_2 \rightarrow 2RO \rightarrow$ products.[1] This makes the study of such radicals of relevance to the use of ethanol as a fuel. Three isomeric radicals may be formed by loss of a hydrogen atom from ethanol

$$C_2H_5OH \rightarrow CH_3CHOH + H \qquad (1)$$

$$C_2H_5OH \rightarrow CH_2CH_2OH + H \qquad (2)$$

$$C_2H_5OH \rightarrow CH_3CH_2O + H \qquad (3)$$

The radicals obtained from reactions 1, 2, and 3, the 1-hydroxyethyl, 2-hydroxyethyl, and ethoxy radicals respectively, have been the subject of a number of experimental and theoretical investigations. The relative stabilities of these radicals have been estimated from calculated heats of formation. In the work of Sosa and Schlegel[2] the heats of the $OH + C_2H_4$ reactions which give rise to the above isomeric C_2H_5O radicals have been calculated using equilibrium geometries optimized at the Hartree−Fock level using 3-21G and 6-31G* basis sets. For CH_3CHOH, CH_2CH_2OH, and CH_3CH_2O respectively, the calculated heats of reaction were −34.7, −27.6, and −29.3 $kcal{\cdot}mol^{-1}$ at the MP4/6-31G** level using HF/6-31G* equilibrium geometries. More recently, an extensive *ab initio* molecular orbital study of the C_2H_5O isomers and their cations has been carried out at the G2 level[3] by Pople et al.[4] This work reports calculated G2 heats of formation of CH_3CHOH, CH_2CH_2OH, and CH_3CH_2O at 298 K as −12.9, −5.9, and −3.1 $kcal{\cdot}mol^{-1}$, respectively. The experimental heats of formation at 298 K of CH_3CHOH, CH_2CH_2OH, and CH_3CH_2O are −15.2 ± 1.0, −13.5 ± 3.0, and −3.7 ± 0.8 $kcal{\cdot}mol^{-1}$ respectively, as determined from measured bond dissociation energies.[5,6] The adiabatic ionization energy of the 1-hydroxyethyl radical was computed in ref 4 as 6.67 eV at the G2 level. However, a vertical ionization energy for CH_3CHOH was not computed in this study. The adiabatic ionization energy of the ethoxy radical was calculated at the G2 level as 10.32 eV.[4] The first adiabatic ionization energy for CH_2CH_2OH could not be computed as no local minima were found for the singlet cation CH_2CH_2OH structure. However, a G2 adiabatic ionization energy of 7.58 eV was computed for ionization of the 2-hydroxyethyl radical to O-protonated oxirane, a cation which is a minimum energy structure on the $CH_2CH_2OH^+$ surface.

Experimental studies have also been carried out on the C_2H_5O radicals, using a number of spectroscopic techniques. A recent study, employing the technique of hydrogen atom abstraction from ethanol by F atoms has been undertaken by Berkowitz et al.,[7] to generate the C_2H_5O isomers. Photoionization mass spectrometry (PIMS), combined with selective deuteriation of C_2H_5OH, was used to determine the ionization energies of each isomer. The first adiabatic ionization energies of CH_3CHOH and CH_3CH_2O were measured to be <6.85 and 10.29 ± 0.08 eV respectively. A shallow onset in the photoion yield curve for CH_3CHOH^+ limited the accuracy of the measured adiabatic ionization energy and suggested that a substantial structural change occurs on ionization for this radical, consistent with the optimized geometries of the radical and ion at the MP2/6-31G* level.[4] In an attempt to selectively photoionize CH_2CH_2OH,[7] the deuteriated form of ethanol, CD_3CH_2OH, was used as a reactant. This gives CD_2CH_2OH on removal of a deuterium atom by F atoms and $CD_2CH_2OH^+$ on ionization. In this way, an adiabatic ionization energy of <8.35 ± 0.06 eV was determined for CH_2CH_2OH. Berkowitz et al.[7] also report in their study of the $F + C_2H_5OH$ reaction evidence for the formation of vinyl alcohol and acetaldehyde due to successive abstraction of hydrogen atoms from the parent ethanol.

Infrared chemiluminescence has been used to determine the relative rates of hydrogen atom abstraction from ethanol with fluorine atoms.[8] From this study it is expected that the rate constants for formation of CH_3CHOH and CH_2CH_2OH are approximately equal, and greater than the rate constant for formation of CH_3CH_2O. If the following hydrogen abstraction reactions are considered:

$$F + C_2H_5OH \rightarrow CH_3CHOH + HF \qquad (4)$$

$$F + C_2H_5OH \rightarrow CH_2CH_2OH + HF \qquad (5)$$

$$F + C_2H_5OH \rightarrow CH_3CH_2O + HF \qquad (6)$$

the experimental heats of formation $\Delta H_{f(298)}$[5,6,9,10] of the reagents and products can be used to calculate reaction enthalpies as ΔH_4

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[†] Dedicated to Professor S. Nagakura on the occasion of his 75th birthday.

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1996.

S1089-5639(96)01302-3 CCC: $14.00

= −(43.1 ± 1.6), ΔH_5 = −(41.4 ± 3.6) and ΔH_6 = −(31.6 ± 1.4) kcal·mol^{-1}. These values show that, as expected, reaction 4 is the most exothermic.

Thus of the three radicals, the 1-hydroxyethyl radical (CH_3CHOH) is the most stable and the first adiabatic ionization energy of CH_3CHOH is lower than the first adiabatic ionization energies of CH_2CH_2OH and CH_3CH_2O.

The aim of this present work was to study the F + CH_3CH_2OH reaction using He I photoelectron spectroscopy to observe bands associated with the radicals formed by primary hydrogen atom abstraction. In particular, it was hoped to obtain an improved first adiabatic ionization energy of CH_3CHOH.

Experimental Section

All the photoelectron spectra obtained in this work were recorded using He Iα radiation (21.22 eV) on a single detector photoelectron spectrometer designed to study short-lived species in the gas-phase.[11] A flow reactor system described previously[12] was used to study the F + C_2H_5OH reaction, where fluorine atoms were generated by a microwave discharge (2.45 GHz) of a flowing mixture of fluorine in helium (5%; BOC Ltd.). The fluorine atom yield was typically greater than 95% as estimated from the photoelectron spectra. The reagent mixing distance above the photon beam could be varied in the range 0−10 cm, which corresponded to reaction times of approximately 0−5 ms. Typical resolution under normal operating conditions was 25−30 meV as measured for argon (fwhm) ionized with He Iα radiation.

Photoelectron spectra recorded for ethanol (99.7%; Heymann Ltd.) were in good agreement with that published previously[13] and showed no evidence of impurity bands. In this work, of the three primary radicals expected from the F + C_2H_5OH reaction, only the first band of CH_3CHOH was observed and the most intense spectra of this band were recorded at 5 mm reagent mixing distance above the photon beam.

Spectral calibration was achieved using the first band of ethanol,[13] the first band of the methyl radical,[14] and the band associated with He II ionization of helium. The band associated with CH_3CHOH was not overlapped by any other bands, and the first band of ethanol recorded with He Iβ radiation proved useful as an additional calibrant.

Results and Discussion

The photoelectron spectrum obtained from the reaction of fluorine atoms with ethanol, recorded in the ionization energy region 5.0−11.0 eV, is shown in Figure 1.

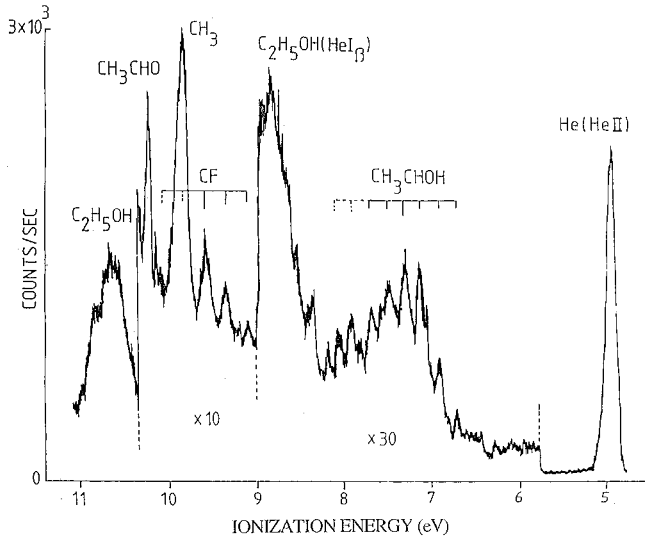

Figure 1. HeI photoelectron spectrum obtained from the reaction of fluorine atoms with ethanol at a reagent mixing distance of 5mm above the photon beam.

In this figure the sharp band at an apparent ionization energy of 4.99 eV is associated with He ionized by He II radiation. Also, the band in the ionization energy range 10.0−11.0 eV (vertical ionization energy 10.62 ± 0.02 eV) can be readily assigned to the first photoelectron band of ethanol[13] and the band in the ionization energy range 8.2−9.1 eV is the first band of ethanol recorded with He Iβ radiation. The sharp band at (9.84 ± 0.02) eV was observed on reaction and was assigned to the first band of the methyl radical.[14] Bands associated with CF (vertical ionization energy 9.55 eV),[15] CO (vertical ionization energy 14.02 eV),[16] and acetaldehyde (vertical ionization energy 10.26 eV)[13] were also observed on reaction. A weak band associated with a short-lived reaction product was also observed in the 6.5−8.5 eV ionization energy range with a vertical ionization energy of (7.29 ± 0.03) eV.

In order to obtain a qualitative picture of the overall course of the F + CH_3CH_2OH reaction, a mixing distance plot was constructed from spectra recorded at constant reagent partial pressures but different mixing distances above the photon beam (see Figure 2). The range of mixing distances studied was 0−10 cm, and the normalized intensity of the most intense band of each species was plotted against mixing distance to obtain this figure. As can be seen from Figure 2, the band at 7.29 eV (labeled as CH_3CHOH) maximizes at ≈5 mm mixing distance. It then decreases to zero intensity at ≈2 cm mixing distance, to be replaced by CF and CH_3CHO which then increase in intensity as the mixing distance increases. The stable products, observed at long mixing distances (>10 cm), are CO and HF (which are not shown in Figure 1 as their first bands occur at higher ionization energies[16,17]). No bands due to vinyl alcohol[19] were observed, although it cannot be ruled out as a secondary reaction product because of overlap of its spectrum with bands of CF and ethanol at short mixing distances (<2 cm) and CF and acetaldehyde at longer mixing distances. Also, the first bands of CH_2CH_2OH and CH_3CH_2O were not observed because they overlapped with the first band of ethanol recorded with He Iα and He Iβ radiation respectively.

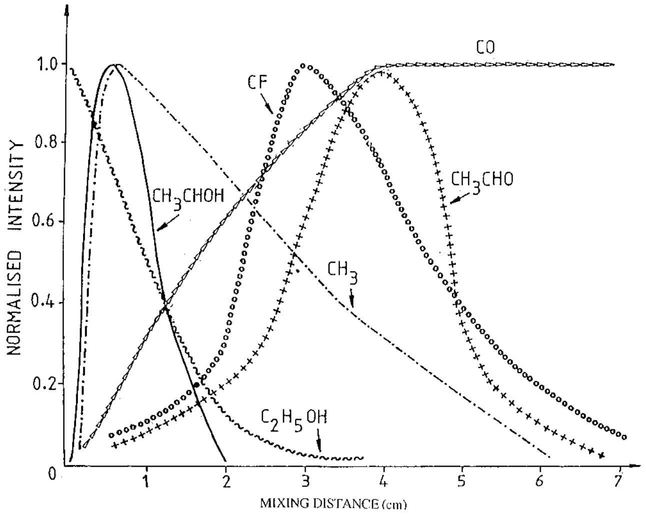

Figure 2. Mixing distance plot showing band intensity variations at constant reagent partial pressures. It should be noted that HF, which was observed as a reaction product at all mixing distances, has been omitted from this plot.

Figure 3 shows an expanded scan of the 5.0−8.0 eV ionization energy range showing the 7.29 eV band. This vibrationally resolved band had an adiabatic ionization energy of (6.64 ± 0.03) eV, a vertical ionization energy of (7.29 ±

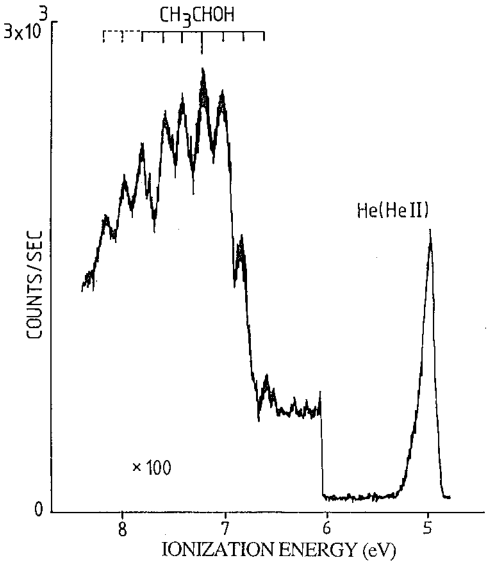

Figure 3. Expanded scan of the 5.0−8.0 eV ionization energy region showing the first photoelectron band of CH_3CHOH.

0.03) eV, and nine vibrational components which form a regular series with a vibrational spacing (1600 ± 30) cm^{-1}. Photoelectron spectra for the reaction of F atoms with fully deuteriated ethanol were also recorded. A similar band associated with a short-lived reaction product was observed centered at 7.29 eV. It also maximized in intensity at a mixing distance of 5 mm above the photon beam and exhibited vibrational structure with an average spacing of (1590 ± 30) cm^{-1}.

On the basis of existing estimates of the first adiabatic ionization energies CH_3CHOH, CH_2CH_2OH, and CH_3CH_2O[4,7] and the result of the mixing distance plot shown in Figure 2, the band in Figure 1 at 7.29 eV is assigned to the first ionization of CH_3CHOH. However, in order to support this assignment, to obtain a computed vertical ionization energy of CH_3CHOH at the G2 level, and determine the vibrational mode associated with the structure in the first band of CH_3CHOH, further *ab initio* molecular orbital calculations were performed on this radical.

At the MP2/6-31G* level, the ground state of CH_3CHOH has a C_1 minimum energy geometry with the electronic configuration $...(12a)^2(13a)^1$. In this work calculations were performed on CH_3CHOH for the neutral ^2A ground state, the singlet ionic state obtained from the $(13a)^{-1}$ ionization, and the triplet state obtained from the $(12a)^{-1}$ ionization. Geometry optimizations followed by frequency calculations were carried out at the MP2(FC)/6-31G* level using the Gaussian 94[20] program at the University of London Computing Centre (ULCC).

A number of C_s structures of the doublet ground state of CH_3CHOH were found to be saddle points. The only true minimum obtained has C_1 symmetry, with a structure in which all the hydrogen atoms are in near-staggered positions. The C−O and C−C bond lengths were calculated to be 1.3807 and 1.4847 Å respectively (in agreement with structure **4a** of ref 4). The vibrational modes, which approximately correspond to C−O and C−C stretching modes, have computed vibrational wavenumber values of 1242 and 1507 cm^{-1} respectively. The singlet cation obtained from the $(13a)^{-1}$ ionization was found to be of C_s symmetry. In this ionic state, the CHOH unit in CH_3CHOH is planar with the hydrogen atoms bonded to the carbon and oxygen atoms lying cis to each other, while the C−H group is staggered with respect to the CH_3 hydrogen atoms. The computed C−O and C−C bond lengths are 1.2700 and 1.4521 Å respectively (in agreement with structure **4c** of ref 4). The C−O stretching mode is computed to have a wavenumber value of 1706 cm^{-1}. None of the normal modes of this ionic state correspond to a pure C−C stretching mode. The computed G2 adiabatic ionization energy for the $(13a)^{-1}$ ionization is 6.67 eV, in agreement with the value quoted in ref 4, and the computed vertical ionization energy is 7.48 eV (with no zero point energy correction). These computed values are in good agreement with the corresponding experimental values of (6.64 ± 0.03) eV and (7.29 ± 0.03) eV. In the ground electronic state of CH_3CHOH the half-filled molecular orbital, the 13a level, consists of essentially a $C(2p\pi)-O(2p\pi)$ antibonding combination. On ionization from this orbital, shortening of the C−O bond is expected to occur with excitation of the C−O stretching mode. This is indeed the case as the major changes upon ionization are calculated at the MP2/6-31G* level to be a shortening of the C−O bond from 1.3807 to 1.2700 Å and a change in the relative positions of the hydrogen atoms. Also, Mulliken analyses of the SCF wave functions of the molecule and ion show that the main changes of electron density that occur on the $(13a)^{-1}$ ionization are on the carbon and oxygen atoms of the C−O bond, and the C−O stretching mode is expected to increase from 1242 to 1705 cm^{-1}. As these calculated wavenumber values are expected to be slightly high, because of only partial allowance for electron correlation at the MP2 level, it is reasonable to assign the resolved structure in the band at 7.29 eV (see Figure 3) to excitation of the C−O stretching mode. The observation that the average vibrational separation decreases only slightly from (1600 ± 30) cm^{-1} to (1590 ± 30) cm^{-1} on going from CH_3CHOH to CD_3CDOD is consistent with this assignment. (In fact, scaling 1705 cm^{-1} by 0.93, a scaling factor suggested in refs 21 and 22 for MP2/6-31G* frequencies, gives 1586 cm^{-1}.)

Calculations at the MP2(FC)/6-31G* level were also performed on the triplet state of CH_3CHOH^+ obtained from the $(12a)^{-1}$ ionization. A number of C_s structures of this state were found to be saddle points, but the true minimum was found to be of C_1 symmetry. The minimum energy structure was found to be similar to that of the neutral radical except the relative orientation of the hydrogen atom bonded to the central carbon atom and the O−H hydrogen atom is trans rather than cis. The C−O and C−C bond lengths were calculated to be 1.3027 and 1.6738 Å and the C−O and C−C stretching modes had wavenumber values of 1399 and 677 cm^{-1} respectively. This triplet state was found to be 4.33 eV above the closed-shell singlet ionic state at their respective minimum geometries, confirming that the ground state of CH_3CHOH^+ arises from the $(13a)^{-1}$ ionization of CH_3CHOH.

The experimental first adiabatic ionization energy (AIE) of CH_3CHOH obtained in this work (6.64 ± 0.03) eV is thus in good agreement with the G2 *ab initio* value of 6.67 eV and is also consistent with the value of <6.85 eV obtained experimentally by PIMS.[7]

This improved AIE may be used with the heat of formation of CH_3CHOH $(\Delta H_f{}^{\circ}{}_{298})$[5,6] of (−15.2 ± 1.0) kcal·mol^{-1} to give $\Delta H_f{}^{\circ}{}_{298}$ of CH_3CHOH^+ as (137.9 ± 1.7) kcal·mol^{-1}. This is turn can be used with the well-established heats of formation of CH_3CHO and H^+ [10] to determine the proton affinity of CH_3CHO as (188.2±1.8) kcal·mol^{-1}, which is slightly high compared with the available experimental values of 185.7 and 186.6 kcal·mol^{-1} [10,24] based on studies of proton transfer reactions. Also, the proton affinity of acetaldehyde has been calculated at the G2 level as 184.1 kcal·mol^{-1} and a lower limit of this value has been determined in the PIMS investigation[7] as (183.8 ± 0.2) kcal·mol^{-1}. Inspection of the values used in the above calculations shows that the value most likely to be slightly in error is the heat of formation of CH_3CHOH as the available experimental $\Delta H_f°_{298}$ values are (-15.2 ± 1.0) and -14.5 kcal·mol^{-1} [5,6] compared with the computed G2 value of -12.9 kcal·mol^{-1}.[4] However, the heat of formation of CH_3CHOH can be reevaluated in the following way. If the proton affinity of CH_3CHO is taken as 186.6 kcal·mol^{-1},[10] then the heat of formation of CH_3CHOH^+ can be evaluated as (139.5 ± 0.2) kcal·mol^{-1} from $\Delta H_f°_{298}$ (H^+) and $\Delta H_f°_{298}$ (CH_3CHO).[10] This value can be combined with the measured AIE of CH_3CHOH of this work ((6.64 ± 0.03) eV) to give $\Delta H_f°_{298}$(CH_3CHOH) as $-(13.6 \pm 0.9)$ kcal·mol^{-1}, which in turn can be used with known values of the heats of formation of H and CH_3CH_2OH[10] to give an improved value of the α(C$-$H) bond energy in CH_3CH_2OH of (94.5 ± 0.9) kcal·mol^{-1}.

At this stage it is convenient to consider Figures 2 and 3 in a little more detail. Figure 2 represents the result of a number of consecutive reactions. The reactions responsible for the production of the molecules observed at >3 cm mixing distance (>1.5 ms reaction time) are not all well established. Also, this figure was compiled using spectral bands which could be clearly identified and assigned. Because of overlapping band problems, particularly at >10 eV ionization energy, not all molecules involved in these consecutive reactions could be observed in the spectra and hence only signals from identified molecules were included in Figure 2.

Nevertheless, it was clear that the CH_3CH_2OH signal disappeared completely after 3 cm mixing distance, with the reactant partial pressures used, because it had reacted completely. CH_3CHOH, the primary product of the F + CH_3CH_2OH reaction, reacts with F atoms to give CH_3CHO. Independent experiments performed as part of this study have shown that this reacts with F atoms to give CH_3CO, which is not seen in this present work because of the large mixing distances and hence reaction times at which CH_3CO is produced. CH_3CO reacts subsequently with F atoms to give HF, CF, and CO as secondary reaction products. (For the first band of CH_3CO, the vertical ionization energy was measured as (8.39 ± 0.05) eV and the band onset was measured as (7.21 ± 0.05) eV. The computed G2 vertical ionization energy and AIE values are 8.39 and 6.66 eV respectively.)

No evidence for "hot" bands in Figure 3 was obtained as the vibrational structure in the first CH_3CHOH band is regular, as far as could be ascertained with the existing experimental resolution. For example, if the first four vibrational components of the CH_3CHOH first band are considered, then if the first component at 6.64 eV was a "hot" band, the first vibrational separation would be less (at $\approx$1240 cm^{-1}) than the next two vibrational separations at (1600 ± 30) cm^{-1}. This was not the case as the vibrational separations were regular at (1600 ± 30) cm^{-1}.

Conclusions

In this work the CH_3CHOH radical, generated as a primary product of the F + C_2H_5OH reaction, has been studied by UV photoelectron spectroscopy and its first adiabatic and vertical ionization energies have been measured.

The values obtained are found to be in agreement with results of previous photoionization mass spectrometry studies[7] and the results of *ab initio* calculations at the G2 level.[4] The experimental vibrational spacings in the first photoelectron band of the CH_3CHOH radical have been assigned, on the basis of the results of the *ab initio* calculations, to excitation of the C$-$O stretching mode in the ground state of the ion. The experimental adiabatic ionization energy (6.64 ± 0.03) eV, when combined with the heat of formation of CH_3CHOH^+, has allowed improved values for the heat of formation of CH_3CHOH and the α(C$-$H) bond energy in CH_3CH_2OH to be obtained.

Acknowledgment. The authors are grateful to the E.P.S.R.C. and the European Community for financial support.

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