Carbon–carbon bond cleavage in the photoionization of ethanol and 1-propanol clusters

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Tunable VUV laser was used to initiate the ion–molecule reactions in the clusters of ethanol and 1-propanol by photoionization in the region between 10.49 to 10.08 eV. Ionic products were detected by the time-of-flight mass spectrometer. In addition to the protonated clusters from proton transfer reactions, the products corresponding to \( \text{carbon–carbon bond cleavage} \) were found to be one of the major products for small sizes of clusters. A comparison with photoionization of methanol clusters and the results of \( \text{ab initio} \) calculation has been made. © 2004 American Institute of Physics. [DOI: 10.1063/1.1704637]

I. INTRODUCTION

Ion–molecule chemistry has been the subject of many studies. In particular, the ion–molecule reactions of lower alcohols have received considerable attention.1–30 A number of experimental studies have focused on the characterizing ion–molecule reactions initiated by the ionization of alcohol in the gas phase,1–15 in clusters,16–27 and in the liquid phase.28–30

Under certain condition following the ionization of a cluster, the reaction products among the ions and molecules within the cluster ion are often similar to the products of the equivalent bimolecular gas-phase ion–molecule reaction. The alcohols are one of the systems that have been shown to have these properties. The products of ion–molecule reactions within the alcohol cluster ions are very similar to the products from the gas phase. Due to the large cross section of proton transfer reaction in the alcohols, the protonated alcohols are the dominant products in both gas phase and cluster reactions. In the gas phase, this has been demonstrated in detail using high-pressure mass spectrometry, tandem mass spectrometry,1–7 and ion cyclotron resonance8–11,13 for methanol and ethanol. It also has been examined for the methanol and ethanol clusters by multiphoton ionization,20–22 electron impact ionization time-of-flight (TOF) mass spectrometry,23–27 and for methanol,16–18 ethanol and butanol18,19 clusters by VUV photoionization mass spectrometry. All of these studies suggested that the protonated alcohols are the dominant ionic products, although some of these protonated alcohol clusters further decompose into protonated ether and water,8 or mixed protonated alcohol–water clusters and ether,20–22,25 No other products have been reported except the minor unreacted ionic clusters, \((\text{ROH})_n^+\).

Using a tunable VUV laser to probe the photofragments,31,32 and to initiate ion–molecule reactions inside clusters17–19 have received an increasing amount of attention in recent years. Tuning the VUV wavelength around the ionization threshold of alcohol clusters allows us to control the reaction energy and study the ion–molecule reaction within the clusters without further breaking them into smaller fragments. In this work, we reported the observation of new ion–molecule reaction channels in ethanol and propanol cluster ions initiated by VUV photoionization. A simple explanation of the reaction mechanism according to the \( \text{ab initio} \) calculation was also presented.

II. EXPERIMENT

The essential elements of the apparatus were a pulsed nozzle, a time-of-flight mass spectrometer, and a VUV pulsed laser. The cluster beam, flight axis, and the VUV laser beam were set such that they were perpendicular to each other. Utrapure He gas (99.9999%) at a pressure of 500 Torr flowed through a reservoir filled with liquid alcohol at room temperature. The gas saturated in alcohol vapor at 297 K was then expanded through a 500 μm diam pulsed nozzle. Alcohol clusters were generated by adiabatic expansion through the nozzle. After skimming by two conical skimmers in different pumping regions, the beam was introduced into the ionization region of the time of flight mass spectrometer, placed 10 cm downstream of the nozzle. The molecular beam

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had a pulsed duration of 700 µs and a diameter of 2 mm. Ions were generated by the photoionization of a pulsed VUV laser beam, accelerated in a Wiley-McLaren-type double electrostatic field to 1.9 keV, and then directed into an 80 cm long field-free flight tube. The ions were detected by a chevron microchannel plate (MCP) detector. After amplification of the signal by a fast preamplifier, the mass spectrum was recorded by a digital oscilloscope and an ion counter.

The VUV laser beam was generated either by frequency tripling of the third harmonic of a Q-switched Nd:YAG laser, or by four wave mixing of UV and near infrared laser beams from a Ti:Al₂O₃ laser system in a rare gas cell. A 355 nm laser beam with 30 mJ/pulse from the third harmonic of an Nd:YAG laser (Spectra Physics GCR 190, 30 Hz, 5 ns pulse duration) was focused by a lens (f = 25 cm) into a rare gas cell filled with 20 Torr of Xe to generate 10.49 eV VUV photons. The generated VUV laser beam had a pulse duration of 4 ns and photon number of 10⁸–10⁹ photon/pulse. For the generation of the other VUV photon energies (10.24–10.04 eV), an UV laser beam (212–216 nm with 10 mJ/pulse, 2 ns pulse duration) from the fourth harmonics of a Ti:Al₂O₃ laser system and a near infrared laser beam (30 mJ/pulse, 2 ns pulse duration, 818–864 nm) from the same laser system were used. These two laser beams were combined together by dielectric coated mirrors and then focused by a lens (f = 25 cm) into a gas cell filled with 100 Torr of Kr. The pulse duration of the VUV laser beam generated by this method was less than 2 ns and the photon number was 10⁶–10⁷ photon/pulse.

After the generation of the VUV laser beam in the rare gas cell, the coaxial UV, near infrared and VUV laser beams were sent to a homemade vacuum monochromator which separates the VUV laser beam from the UV and near infrared laser beams. The distance between the laser focal point in the rare gas cell and the grating in the vacuum monochromator was set to be 100 cm. A concave grating with 1200 l/mm and radius of 98.5 cm (Richardson Grating Laboratory) was used in the monochromator. The concave grating refocused the expanding VUV radiation into the cluster beam, which is 100 cm away from the grating. The separation distance between the VUV laser beam from the other laser beams at the ionization region was very large (>4 cm) and only the VUV laser beam was sent to the ionization region of the time-of-flight mass spectrometer. The grating was set in the near-normal incidence (15°) and the first order of the VUV radiation from the grating was used. Since the VUV laser bandwidth (<1 cm⁻¹) was much smaller than the spectral resolution of the monochromator, the VUV beam size was not affected by the dispersion of the grating. It only depends on the UV/near infrared laser beam sizes and the focal lengths of both the concave grating and lens. We estimated that the VUV beam size was less than 0.5 mm in the ionization region.

In order to eliminate the effect from the impurity, brand new chemicals purchased from various companies were used. C₂H₅OH was purchased from Aldrich (HPLC grade) and Fluka (HPLC grade, ≥99.8%), C₂D₅OH from Cambridge Isotope (98%), and 1-propanol from Aldrich (HPLC grade, 99.5%) and Acros (≥99.5%). These chemicals were used directly without further purification.

### III. COMPUTATIONAL METHOD

All ab initio calculations were done with the GAUSSIAN 98 program. The geometry optimization and vibrational frequencies of the reactants and products were calculated by using Becke3LYP level with 6-31+G*. To establish a more reliable energy results, single point calculations were performed at the B3LYP/aug-cc-pVTZ level using the B3LYP/6-31+G* equilibrium geometries.

### IV. RESULTS

The time-of-flight mass spectrum of ethanol clusters ionized by VUV photons at 10.49 eV is shown in Fig. 1(a). Four series of cluster ions were observed in this VUV photon energy region: protonated ethanol cluster ions, (EtOH)ₙH⁺ for n = 1–15; nonreacted cluster ions, (EtOH)ₙ⁺ for n = 1,2; mixed protonated water–ethanol cluster ions, (EtOH)ₙH₂O⁺, for n = 4–15; and mixed protonated formaldehyde–ethanol cluster ions, (EtOH)ₙCH₂OH⁺, for n = 1,2. The mixed protonated water–ethanol cluster ions have very small intensities and they are not easy to be seen in the

![FIG. 1. The time of flight mass spectrum of ethanol clusters ionized by (a) 10.49 eV (b) 10.2 eV photons. The sequence a, b, c correspond to (C₂H₅OH)ₙH⁺, (C₂H₅OH)ₙ⁺, and (C₂H₅OH)ₙCH₂OH⁺, respectively.](image-url)
ions are observed: protonated propanol cluster ions, 

The intensity of the mixed protonated formaldehyde–ethanol cluster ions for \( n = 1 \) is as large as the protonated ethanol monomer and dimer ions. The deuterium labeled ethanol, \( \text{C}_2\text{D}_5\text{OH} \), was also studied. For the products corresponding to the \( \beta \) carbon–carbon bond cleavage, only \((\text{CD}_2\text{O})(\text{C}_2\text{D}_5\text{OH})_n\text{H}^+\) was observed. This indicates that the \( \beta \) carbon–carbon bond cleavage occurs at a rate faster than any hydrogen–deuterium scrambling in the cluster ion. Note that the VUV photon energy (10.49 eV) is only 0.02 eV above the ionization potential (10.47 eV) of the ethanol monomer. This excess energy is not large enough for the monomer ions to dissociate and produce fragment ions. The two lowest dissociation thresholds of the ethanol ion are 10.8 eV for the reaction of \( \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4\text{O}^+ + \text{H} \) and 11.25 eV for the reaction of \( \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_2\text{OH}^+ + \text{CH}_4 \). At the 10.49 eV photon energy, it is therefore not possible to have reactions between the fragment ions and ethanol in the clusters. Furthermore, the VUV photon energy is tuned between 10.49 and 10.08 eV which is below the ionization potential of the monomer. The results are very similar to the result at 10.49 eV, except some difference at the intensities of monomer and small cluster ions. Figure 1 shows the time of flight mass spectrum of ethanol clusters ionized by VUV photons at 10.2 eV. Ethanol monomer ion disappears because the VUV photon energy is smaller than the ionization energy, and the intensity of protonated ethanol monomer ion becomes very small. The intensity ratio between \((\text{CH}_3\text{OH})_2\text{H}^+ : (\text{CH}_2\text{OH})\text{CH}_2\text{OH}^+\) also changed from 1:40 at 10.49 eV to 1:3 at 10.2 eV. The more unprotonated clusters is expected at lower ionization energy. In addition, the intensity of protonated formaldehyde–ethanol becomes very large at low photon energy.

The mass spectrum of 1-propanol clusters ionized by the VUV laser beam is shown in Fig. 2. The ionization threshold of the 1-propanol monomer is 10.22 eV, and the first two dissociation channels of the 1-propanol cation are \( \text{C}_3\text{H}_7\text{OH} \rightarrow \text{C}_3\text{H}_6\text{O}^+ + \text{H}_2 \) at 10.6 eV and \( \text{C}_3\text{H}_7\text{OH} \rightarrow \text{C}_3\text{H}_6\text{O}^+ + \text{H} \) at 10.7 eV. The VUV photon energy was tuned to straddle the monomer ionization threshold (10.49–10.01 eV), and the results for each photon energy are similar. Five series of cluster ions are observed: protonated propanol cluster ions, \((\text{CH}_3\text{OH})_n\text{H}^+\) for \( n = 1–20 \); nonreacted cluster ions, \((\text{CH}_3\text{OH})_n\) for \( n = 1,2 \); mixed protonated water–propanol cluster ions, \((\text{CH}_3\text{OH})(\text{CH}_2\text{OH})_n\text{H}^+\) for \( n = 9–19 \); mixed protonated formaldehyde–propanol cluster ions, \((\text{CH}_3\text{OH})_n\text{CH}_2\text{OH}^+\) for \( n = 1–3 \); and mixed protonated methanol–propanol cluster ions \((\text{CH}_3\text{OH})(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_n\) for \( n = 1,2 \). Except for mixed protonated water–propanol cluster ions which the intensities are too small to be shown in the figure, all the other series of cluster ions are clearly shown in the figure. The first three series are equivalent to the products of methanol clusters ionized by UV multiphoton or electron impact. The last two series correspond to the products of \( \beta \) carbon–carbon bond cleavage. For \( n = 1 \) of mixed protonated formaldehyde–propanol cluster ions, the intensity is also very large. For the mixed methanol–propanol cluster ions, \((\text{CH}_3\text{OH})(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_n\), we believe that it originates from hydrogen atom transfer between two dissociating fragments when \( \beta \) carbon–carbon bond cleavage occurs. These signals could not be due to the \( ^{13}\text{C} \) isotope of the protonated formaldehyde–propanol clusters. The ratio of mass intensity \( m = 92/m = 91 \) is about 14%, which is larger than the natural abundance of \( ^{13}\text{C} \) (4.4% for the total of four carbon atoms) by more than a factor of 3. In addition, scanning the delay time of the VUV laser pulse with respect to the cluster pulse also demonstrates that mass 92 ions and mass 91 ions originate from different reactants. For a pulsed cluster beam, the cluster sizes close to the front and the end of the pulse are smaller than the cluster sizes in the center of the pulse. This is because the molecular intensity at the center of the pulse reaches its maximum value due to the full open of the nozzle. The large clusters are easier to be generated at high molecular intensity in the center of the pulse than under low molecular beam intensity at both ends of the pulse. The intensity ratio of mass 91 ions to 92 ions in 1-propanol clusters was found to change with the delay time of pulsed nozzle, as shown in Fig. 3. The large ion intensity ratios of \( m/e = 92: m/e = 91 \) at the front (180–320 \( \mu \text{s} \)) and the end (700–850 \( \mu \text{s} \)) of the cluster beam suggest most of ions \( m/e = 92 \) come from small size of clusters. On the other hands, small ion intensity ratios of \( m/e = 92: m/e = 91 \) at the center (350–450 \( \mu \text{s} \)) of the cluster beam indicate that large clusters have more contribution to ion \( m/e = 91 \) than to ion \( m/e = 92 \). The change of intensity ratio of \( m/e = 92: m/e = 91 \) with delay time of pulsed nozzle simply means they represent two different reactions.

We consider unlikely possibility that these new reactions we observed come from an impurity of formaldehyde and acetaldehyde that might be embedded in our sample. The samples we used are all new and of extra pure quality, and
the impurities indicated on the labels do not show formaldehyde in ethanol and 1-propanol. We also checked the impurity of the sample using GC mass spectrometer. If there were impurities, they would be less than 2% according to the S/N ratio of the GC mass spectrum. In order to investigate the impurity effect, 5% of formaldehyde was added to the ethanol. The TOF mass spectrum of 5% formaldehyde in ethanol obtained by VUV photoionization at 10.49 eV was compared to that of pure ethanol under the same conditions.

Figures 4a and 4b show the TOF mass spectrum of 5% formaldehyde in ethanol and spectrum of pure ethanol, respectively. Both of them show the similar protonated ethanol cluster distribution. In addition, the intensities of mixed protonated formaldehyde–ethanol cluster ions also have the similar intensity distribution. They are not affected by the 5% of formaldehyde in ethanol. The effect of 5% formaldehyde was only shown in the peaks of m/e = 61, 89, and 90. The lack of effect on protonated formaldehyde–ethanol cluster from 5% formaldehyde as well as no intensity of m/e = 61, 89, and 90 observed in the pure ethanol spectrum further confirm that the mixed protonated formaldehyde–ethanol cluster ions we observed in the pure ethanol mass spectrum do not come from the impurity of formaldehyde.

A similar argument is applied to another new reaction channel of 1-propanol, which produces methanol-1-propanol cluster-ions. If methanol-1-propanol cluster ions were from the impurity of methanol in 1-propanol, the protonated methanol-1-propanol cluster ions would have appeared in the spectrum due to the large cross section of proton transfer reaction. Indeed, by adding a small amount of methanol in 1-propanol, the protonated methanol-1-propanol cluster ions at mass = 93, and 153 displayed very large intensities. However, the mass spectrum of pure 1-propanol only have unprotonated mixed methanol-1-propanol cluster ions, no protonated mixed cluster ions were observed. This confirms that the products are from the proposed reaction channels, and not from the impurity of methanol in 1-propanol.

V. DISCUSSION

The new ion–molecule reactions we observed in ethanol and 1-propanol can be summarized as follows:

\[
(C_2H_5OH)_{n}^+ \rightarrow (C_2H_5OH)_{n-1}(CH_2O)H^+ + CH_3 + mC_2H_5OH, \tag{1}
\]

\[
(1-C_3H_7OH)_{n}^+ \rightarrow (1-C_3H_7OH)_{n-m-1}(CH_2O)H^+ + C_2H_5 + m(1-C_3H_7OH), \tag{2}
\]

\[
(1-C_3H_7OH)_{n}^+ \rightarrow (1-C_3H_7OH)_{n-m-1}(CH_2O)H^+ + C_2H_5 + m(1-C_3H_7OH). \tag{3}
\]
TABLE I. Heats of reactions obtained from ab initio calculation with B3LYP/6-31G**.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>ΔH (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH(_3)OH)(_2)→(CH(_3)OH)(^+)+e(^-)</td>
<td>9.05</td>
</tr>
<tr>
<td>(CH(_3)OH)(_2)→CH(_3)OH+CH(_3)OH+e(^+)</td>
<td>10.05</td>
</tr>
<tr>
<td>(CH(_3)OH)(_2)→(CH(_3)OH-CH(_3)OH)+H+e(^-)</td>
<td>10.12</td>
</tr>
<tr>
<td>(CH(_3)OH)(_2)→CH(_3)OH+CH(_3)O+e(^-)</td>
<td>10.38</td>
</tr>
<tr>
<td>(C(_2)H(_4)OH)(_2)→(C(_2)H(_4)OH)(^+)+e(^-)</td>
<td>8.6</td>
</tr>
<tr>
<td>(C(_2)H(_4)OH)(_2)→(C(_2)H(_4)OH)+CH(_3)+e(^-)</td>
<td>9.32</td>
</tr>
<tr>
<td>(C(_2)H(_4)OH)(_2)→C(_2)H(_4)OH+C(_2)H(_4)OH+e(^-)</td>
<td>9.7</td>
</tr>
<tr>
<td>(C(_2)H(_4)OH)(_2)→C(_2)H(_4)O+C(_2)H(_4)OH(^+)+e(^-)</td>
<td>9.8</td>
</tr>
<tr>
<td>(1-C(_2)H(_4)-OH)(_2)→(C(_2)H(_4)-OH-CH(_3)-OH)+C(_2)H(_4)+e(^-)</td>
<td>9.25</td>
</tr>
<tr>
<td>(1-C(_2)H(_4)-OH)(_2)→(C(_2)H(_4)-OH-CH(_3)-OH)+C(_2)H(_4)+e(^-)</td>
<td>9.57</td>
</tr>
</tbody>
</table>

A simple explanation for the occurrence of these new reaction channels is following. The electron that belongs to the long pair of the oxygen atom is removed when the alcohol molecule is ionized. The oxygen atom therefore becomes chemically similar to a nitrogen atom and prefers to form three chemical bonds. When a new bond is formed between an adjacent C atom and the O atom, it weakens the β carbon–carbon bond and result in the cleavage of this bond. The lack of C–H bond cleavage probably results from the difference of the bond strength between C–H bond and C–C bond. A similar argument can also apply to the methanol clusters, where only the C–H bond could cleave and produces protonated formaldehyde–methanol cluster ions. In fact, we do observe protonated formaldehyde–methanol cluster ions when methanol clusters are ionized at 10.49 eV, which is below the ionization threshold of methanol monomer. However, the intensity is approximately two to three orders of magnitude less than the protonated methanol clusters. The small intensity of the mixed formaldehyde–methanol clusters must be due to the stronger C–H bond strength in methanol than the C–C bond strength in ethanol.

This reaction mechanism is supported by the ab initio calculation. The heats of reactions for various dissociation channels of ethanol dimer obtained by ab initio calculations are listed in Table I. There are two pathways for the proton transfer reaction. One pathway is the production of ethoxy radical and protonated ethanol. It has the highest dissociation threshold of 9.8 eV. The other dissociation channel corresponding to the proton transfer produces 1-hydroxy ethyl radical and and protonated ethanol. This channel has a dissociation threshold of 9.7 eV. However, the channel with the lowest dissociation threshold corresponds to the CH\(_3\) elimination, due to the weak β carbon–carbon bond. It is only 9.32 eV. The dissociation threshold difference between β carbon–carbon bond cleavage and proton transfer reactions is at least 0.38 eV, which is larger than the uncertainty of the calculation. Although the calculation was only performed for the dimer, it does not reflect the entire picture of the experimental results. However, these thresholds would gradually decrease with the increase of cluster sizes because the solvation energy of cation is larger than that of neutral species. As a result, the calculation suggests at least that these channels are all accessible for all cluster sizes at the photon energy we used.

The low dissociation threshold of β carbon–carbon bond cleavage makes the protonated formaldehyde–ethanol cluster ions to be one of the major products. The high dissociation threshold of the proton transfer reaction also explain why the intensity of protonated ethanol monomer decreases rapidly compared to that of protonated formaldehyde–ethanol cations as the VUV photon energy decreases from 10.49 to 10.2 eV. On the other hand, the intensity of protonated ethanol monomer becomes the major channel at high photon energy. This provides a reasonable explanation that the protonated clusters are the major products observed in electron impact ionization. Some of the heats of reactions for 1-propanol dimer dissociation channels are listed in Table I. The low dissociation thresholds of these reactions indicate the easy generation of the corresponding products using VUV photon in the energy region between 10–10.5 eV.

The ion molecular reactions of methanol clusters have been studied extensively. It is thus interesting to compare the photoionization of methanol clusters to that of ethanol clusters. The heats of reactions of methanol dimer for various dissociation channels are also listed in Table I. In contrast to the energy diagram which both of the proton transfer reactions have reaction thresholds higher than that of β carbon–carbon bond cleavage channel in ethanol dimer, one of the proton transfer channels in methanol dimer has the lowest threshold and thus it is expected to be the major channel at low energy. In fact, it has been shown that the proton transfer reaction with the lowest threshold is the dominant channel at low photon energy, and the other proton transfer reaction with higher reaction threshold becomes the major channel at high photon energy, respectively. Consequently, the branching ratio of the β carbon–hydrogen bond cleavage channel of methanol dimer is small due to the competition with these proton transfer reactions.

The products corresponding to the β carbon–carbon cleavage indeed have been observed from the photoionization of ethanol and butanol clusters and ion–molecule reactions of ethanol in gas phase with a relatively large intensity in previous studies. However, a lot of fragments, like H\(^+\), CH\(_2\)\(^+\), CHO\(^+\), CH\(_2\)O\(^+\), CH\(_2\)OH\(^+\), C\(_2\)H\(_3\)\(^+\), C\(_2\)H\(_4\)\(^+\) of ethanol and like C\(_2\)H\(_2\), CH\(_2\)OH\(^+\), C\(_3\)H\(_5\), C\(_2\)H\(_4\)O\(^+\), C\(_2\)H\(_5\)O\(^+\), C\(_2\)H\(_6\)O\(^+\) of butanol were also produced in these experiments. These fragments were generated because of the large excess energy left after electron impact ionization. They could also be produced by UV multiphoton absorption due to the existence of the intensive UV laser beam in the VUV photoionization region. For example, the UV laser beam could propagated coaxially with the VUV laser beam and reached the ionization region if the UV laser beam was not separated from VUV laser beam after it was used to generate the VUV laser beam. As a result, the products corresponding to the β carbon–carbon cleavage in these studies were either attributed to the reactions of these fragments with alcohols, or they were treated as a background and no explanation was given. In fact, some of the products corresponding to the carbon–carbon bond cleavage observed in previous studies could be attributed to the reaction mechanism we proposed in this work.

In conclusion, we demonstrated that the photoionization
products of alcohol clusters corresponding to the $\beta$ carbon–
carbon cleavage could have intensity as large as protonated
alcohols at small sizes of clusters. Since the UV laser beam
was separated from the VUV laser beam and the VUV pho-
tons with energies smaller than the dissociative ionization
threshold of alcohol monomer were used in our experiment,
no fragments were produced and therefore the interference of
fragments can be completely excluded. This “soft” ioniza-
tion techniques reveals information which is not easy to be
previously reported experiments, the high energy in the ion-
ization of the alcohol clusters increases substantially the pro-
ton transfer rate, resulting in the protonated alcohol cluster
ions as the dominant products.

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