Ultrafast Proton Transfer Dynamics on the Repulsive Potential of the Ethanol Dication: Roaming-Mediated Isomerization versus Coulomb Explosion

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ABSTRACT: If a molecular dication is produced on a repulsive potential energy surface (PES), it normally dissociates. Before that, however, ultrafast nuclear dynamics can change the PES and significantly influence the fragmentation pathway. Here, we investigate the electron-impact-induced double ionization and subsequent fragmentation processes of the ethanol molecule using multiparticle coincident momentum spectroscopy and ab initio dynamical simulations. For the electronic ground state of the ethanol dication, we observe several fragmentation channels that cannot be reached by direct Coulomb explosion (CE) but require preceding isomerization. Our simulations show that ultrafast hydrogen or proton transfer (PT) can stabilize the repulsive PES of the dication before the direct CE and form intermediate H2 or H2O. These neutrals stay in the vicinity of the precursor, and roaming mechanisms lead to isomerization and finally PT resulting in emission of H3+ or H3O+. The present findings can help to understand the complex fragmentation dynamics of molecular cations.

INTRODUCTION

The removal of two electrons from a neutral molecule is a process of fundamental interest in chemical physics. An understanding of the structure of molecular dications and the dynamics of dissociation processes is relevant to understand and model the behavior of gaseous plasmas as well as the ionosphere and astrophysical environment.1−3 Significant rearrangement of the chemical bonds can be initiated due to the considerable internal energy in the dications, leading to various Coulomb explosion (CE) channels.3,4 Of particular interest in the present work are the very fast hydrogen and proton transfer mechanisms (for general discussion, we use PT to represent both hydrogen and proton transfer) that are relevant in various fields of physics, chemistry, and biology.5−7 In particular, PT is a common and fundamental process in organic chemistry and molecular biology as all organic compounds contain a large fraction of hydrogen atoms.8 PT can form different isomers and therefore change functional properties of the molecule. In particular, proton-translocating tautomerization of DNA base pairs has been suggested as a cause of mutations, which have been broadly studied in the past 50 years.9−13

PT-initiated isomerization of a molecule affects chemical reactions in solution. A changing chemical environment of a biomolecule can induce conformational or isometric transformations.3 Recently, it was found for amino acids that the intramolecular PT from the carboxyl (−COOH) group to the amino (−NH2) group will reduce the molecule’s total energy in aqueous solution or in crystals and form a so-called “zwitterion”.14 As being the lightest element, hydrogen exhibits ultrafast dynamics whether in classical migration15−17 or being subject to nuclear quantum effects.18−20 For example, in ionized glycine, the timescale of PT was determined to be less than 50 fs.16 In a recent work, Richter et al. showed that intermolecular PT is fast enough to influence the electronic decay due to the coupling of the electron and nuclear dynamics in water clusters.21 Even on the repulsive PES of the dication where the system is expected to rapidly dissociate, PT can stabilize the dication. For example, Maclot et al. showed for double ionization of glycine that CE competes with ultrafast intramolecular PT evolving within ~30 fs resulting in stable glycine dication.15

On the other hand, PT can lead to isomerization during molecular fragmentation.22,23 As a prototype, the PT in acetylene has been studied by pump-probe experiments,24 X-ray core−shell ionization,25 and α-particle irradiation.26 Furthermore, if a process involves multiple PT,9,27 more complex fragments can be formed like H3+ emitted from organic molecules.28−32 In this respect, Ekanayake et al. have...
performed time-resolved pump-probe experiments using femtosecond laser pulses and ab initio molecular dynamics (AIMD) simulations. For different alcohols, they found that, for $H_3^+$ production, the intermediate roaming of $H_2$ plays an important role and that the timescale for the fragmentation process is between 100 and 260 fs.30,32 The calculation of the respective reaction pathways is challenging for conventional transition-state (TS) theory since $H_2$ roaming may explore large regions of the PES and bypass saddle points entirely.33

In the present work, we carry out combined experimental and theoretical studies concerning the PT-induced isomerization and CE of the ground-state ethanol dication. Fragment ion and electron momentum spectroscopies, accompanied by molecular dynamics calculations, allow us to directly identify the different fragmentation channels and understand the underlying mechanisms and the role of PT. It is found that, while double ionization leads to a repulsive PES, fast PT can stabilize the dication before CE and then open several isomerization channels. Here, we focus on three channels, including one CE channel and two isomerization channels, for emission of $H_3^+$ and $H_2O^+$:

$$\text{CH}_3\text{CH}_2\text{OH}^2+ \rightarrow \text{CH}_3^+ + \text{CH}_2\text{OH}^+$$ (1)
$$\text{CH}_3\text{CH}_2\text{OH}^2+ \rightarrow H_3^+ + \text{C}_2\text{H}_5\text{O}^+$$ (2)
$$\text{CH}_3\text{CH}_2\text{OH}^2+ \rightarrow H_2\text{O}^+ + \text{C}_2\text{H}_5^+$$ (3)

The theoretical analysis of the molecular dynamics using the AIMD simulation and the static energy calculation of PESs and TSs shows that all three channels are open on the ground-electronic-state PES of $\text{CH}_3\text{CH}_2\text{OH}^2+$. As the ethanol dication reached in a vertical transition is in a repulsive state along the $C_\alpha-C_\beta$ bond cleavage (carbon connecting to the hydroxyl is defined as $C_\alpha$, while the terminal one is $C_\beta$), it is expected to dissociate via CE. In the same electronic state, however, new fragmentation channels are opened if a stabilization process can take place before CE. There are three possible ways to stabilize the ethanol dication, i.e., PT from $C_\alpha$ to $C_\beta$ ($\text{CH}_3\text{CH}_2\text{OH}^{2+} \rightarrow \text{CH}_3\text{CHOH}^{2+}$), from $C_\alpha$ to hydroxyl ($\text{CH}_3\text{CH}_2\text{OH}^{2+} \rightarrow \text{CH}_2\text{CHOH}^{2+}$ forming an intermediate $\text{H}_2\text{O}$ group), and forming an intermediate $\text{H}_2$ group. The Mulliken charge analysis shows that the intermediates like $\text{H}_2$ and $\text{H}_2\text{O}$ are neutral groups. Their long-time motion around the parent molecule can be regarded as a roaming chemical process.33,34 We demonstrate that the intramolecular PT and roaming dynamics play key roles in stabilizing the ethanol dications and altering significantly the fragmentation pathways.

## RESULTS

The experiments were performed by electron-impact ionization of ethanol using two different spectrometers at similar impact-energies of 91 and 100 eV (see Supporting Information for details). The dissociative CE channels were identified by analyzing the ion-ion time correlation map of both ions detected on a time- and position-sensitive detector. In the diagram shown in Figure 1a, the time of flight (TOF) of the first detected ion is plotted against the ion detected first. Sharp coincidence lines with a slope of $-1$ are observed for channels 1–3 (purple-shaded labels) confirming that these are pure two-body dissociation processes. For all other channels labeled in Figure 1a, the ethanol dications dissociate into three or more fragments including two ions and neutrals. The most intense region in the center of Figure 1a originates from reactions similar to channel 1 but with hydrogen loss for one or both fragment ions. In addition, there are coincidences for $\text{C}_3\text{H}_3^+ + \text{H}_2\text{O}^+ + n\text{H}$ ($n = 1, 2$), again with one or two neutral hydrogens emitted. Finally, there are three-body channels including a $\text{H}_4^+$ ion with $n = 1–3$ in the time-of-flight interval of the first detected ion between 1 and 2.2 $\mu$s. The corresponding coincidence lines are broad and strongly overlapping along the $y$ axis since the undetected neutral fragment is rather heavy and carries considerable momentum. In an earlier ion-ion coincidence measurement for ethanol using intense infrared laser pulses for ionization, more pure two-body fragmentation channels without neutral hydrogen loss were found than in the present measurement.35 The reason most likely is that strong field double ionization evolves as sequential single ionization from the outermost valence electrons. For the present particle-impact ionization, both electrons are removed simultaneously and not necessarily from the outermost shell such that more internal energy is present in the dication that can lead to the emission of neutrals. In the following, we will concentrate our discussion to the two-body channels 1–3.

In one of our measurements, one of the final state electrons was detected in coincidence with the two ions. Thus, the projectile energy loss spectra for the different fragmentation channels were obtained (Figure 1b). The spectra show onsets at about 28 eV for all three channels, meaning that these are initiated by the removal of two electrons from the outermost
The range marked in yellow indicates the energy region for a vertical ionization from the neutral ground state to the dicaticonic ground state of ethanol. The AIMD simulations (see Supporting Information for details) show that the two-body CE process is dominated by channel 1 that contributes about 18.2% to the total simulated trajectories. For channel 2, the branching ratio is 2.6%, and only three out of 2000 trajectories ended up in channel 3. For all of the calculations, the charge states of final fragments are obtained from the Mulliken population analysis, which confirms that the studied channels produce two cations. The simulated and experimental kinetic energy release (KER) distributions presented in Figure 1c show good agreement within the limited statistical significance of the trajectory number.

The fragmentation dynamics of the CE channel 1 is shown in Figure 2. Panel (a) presents the center-of-mass (COM) distance between CH$_3^+$ and CH$_2$OH$^+$ as a function of time. This diagram shows two main features: (i) most of the molecules start to dissociate directly within 50 fs, giving rise to the red region formed by a large number of trajectories; (ii) a small fraction shows dissociation after some time delay ranging from several tens of femtoseconds to more than 500 fs. During this time, there is vibration between the two subunits manifesting in the oscillations of the blue and red curves in the inset of Figure 2a. To form the long-lived dications, a fast (less than 50 fs) stabilization mechanism is required, which is exactly the ultrafast hydrogen migration. The insets in panel (a) show three typical trajectories corresponding to three mechanisms indicated by green, blue, and red curves: (i) fast CE (FCE) where the two charged fragments dissociate directly once a dication is formed; (ii) delayed CE with one hydrogen exchange (DCE-H1); and (iii) delayed CE with two hydrogen exchange (DCE-H2). For DCE-H1, one hydrogen transfers from C$_\alpha$ to C$_\beta$ in the first step, and subsequently, the identical one transfers back to C$_\alpha$ before C$_\alpha$–C$_\beta$ breakage. For DCE-H2, however, another hydrogen belonging to C$_\beta$ in the neutral ethanol transfers back to C$_\alpha$ in the second step.

The detailed analysis of the simulated fragmentation dynamics shows that dissociation through the DCE-H1 mechanism is statistically faster than DCE-H2 as depicted by their COM distances as a function of time in Figure 2b,c, respectively. For DCE-H1, the C$_\alpha$–C$_\beta$ bond starts to dissociate before about 300 fs. For DCE-H2, however, the lifetime is longer than 300 fs for most of the cases. The intermediate steps of the two fragmentation pathways are shown in Figure 2d,e. For both mechanisms, the ultrafast hydrogen exchange is completed within about 20 fs. The lifetime difference of DCE-H1 and DCE-H2 is due to the different orientations of the transferred or exchanged hydrogen (defined as H$_1$ shown by the pink ball in Figure 2d or H$_2$ by the green one in Figure 2e) relative to the C$_\alpha$–C$_\beta$ bond. For DCE-H1, the angle $\angle$H$_1$C$_\alpha$C$_\beta$ is always a pointed angle (<90°). Thus, H$_1$ is always very close to C$_\alpha$ making the back transfer easy to occur. For DCE-H2, the angle $\angle$H$_2$C$_\beta$C$_\alpha$ is an obtuse angle at the very beginning. The hydrogen exchange can occur only after a rotation of the CH$_3$ group relative to the C$_\alpha$–C$_\beta$ bond until reaching a small enough distance between H$_2$ and C$_\alpha$. Figure 2f shows the PESs (see Supporting Information for details) as a function of the C$_\alpha$–C$_\beta$ bond length. The blue arrow in the Franck–Condon region indicates the most probable vertical ionization from neutral to the dicaticonic ground state. Due to the repulsive PES, the dication can dissociate through FCE in principle. On the ground-state
PES of the ethanol dication, however, there are local minimum energy points corresponding to equilibrium geometries. As shown by the red curve in Figure 2f, a bound state is formed if one hydrogen transfers from $C\alpha$ to $C\beta$. The resulting red curve presents a potential energy barrier that is even higher than the most probable vertical transition point. As a result, $\text{CH}_4\text{CHOH}^2+$ does not dissociate via $C\alpha - C\beta$ bond breakage both in experiments and in the simulation. The crossing between the two PESs of $\text{CH}_3\text{CH}_2\text{OH}^2+$ and $\text{CH}_4\text{CHOH}^2+$ forms a TS connecting these two isomers. As the rigid PES scanning freezes all degrees of freedom, such PES may be different from the actual situation of the fragmentation. As shown by the orange curve in Figure 2f, the relaxed PES scanning indicates that there will be isomeric transformation from $\text{CH}_4\text{CHOH}^2+$ to $\text{CH}_3\text{CH}_2\text{OH}^2+$ with increasing $C\alpha - C\beta$ length. The corresponding TS and the pathway are confirmed by the intrinsic reaction coordinate (IRC) calculation as shown in Figure 2g.

For channel 2 with the $\text{H}_3^+$ and $\text{C}_2\text{H}_3\text{O}^+$ fragments, Figure 3 shows the COM distance between these two groups as a function of time. $\text{H}_3^+$ emission appears from $\sim100$ to $\sim500$ fs, which is in agreement with the previous time-resolved pump-probe studies. The trajectory analysis shows that there are five possible ways of forming $\text{H}_3^+$, which all include the formation and subsequent roaming of one intermediate $\text{H}_2$ as shown in Figure 4: $C\alpha$ emits one $\text{H}_2$ molecule, which captures one proton (a) from $C\beta$ or (b) from the hydroxyl group ((c) $C\beta$ as hydrogen and proton donors, (d) $C\beta$ and hydroxyl as hydrogen and proton donors, and (e) $C\alpha$, $C\beta$ and hydroxyl as hydrogen and proton donors forming $\text{H}_3^+$). For all of the cases, ultrafast PT and $\text{H}_2$ formation can occur within about 25 fs, which stabilizes the ethanol dication concerning the $C\alpha - C\beta$ bond breakage. For the reaction channels shown in Figure 4c–e, the dynamics starts by hydrogen transfer from $C\alpha$ to $C\beta$ and is followed by emission of $\text{H}_2$ from the CH$_4$ group. Thus, there are generally two ways to produce the intermediate roaming $\text{H}_2$: (i) the direct formation from $C\alpha$ as shown in Figure 4a,b and (ii) the indirect way from $C\beta$ as shown in Figure 4c–e.

For the first mechanism, roaming $\text{H}_2$ is formed within about 20 fs, and finally, one proton can be captured from the neighboring carbon or hydroxyl before 200 fs. For the second mechanism, however, no proton capture from neighboring carbon is observed. The proton can be captured from the parent carbon ($C\beta$) or from hydroxyl for which rather long-time roaming (longer than 200 fs) is needed. The TS analysis and IRC path calculations confirm the above-simulated pathways. Figure 4f,g shows the pathways corresponding to $\text{H}_2$ formation from $C\alpha$ and $C\beta$ respectively. For the first case, the intermediate $\text{H}_2$ can directly attract one proton from $C\beta$ via TSa-1 $\rightarrow$ TSa-2 or from hydroxyl via TSb. For the second case, however, proton capture can happen only after PT from $C\alpha$ to $C\beta$ as shown by TS-2 in Figure 4g, which is in line with the MD simulations.
Figure 5. Pathways for H$_3$O$^+$ formation dynamics. (a) C$_{\alpha}$ as donor contributes two hydrogens to the final H$_3$O$^+$. (b) Both C$_{\alpha}$ and C$_{\beta}$ are donors, and each contributes one hydrogen to the final H$_3$O$^+$. (c) Potential energy curves as a function of internuclear distance of C$_{\alpha}$-O. (d) Reaction coordinate associates three transition states for H$_3$O$^+$ production. The open circles and star in panel (c) mark the possible transition states. The arrows in panel (d) indicate the main feature of vibration mode. The pink and green hydrogens belong to C$_{\alpha}$ and C$_{\beta}$ in the neutral ethanol, respectively.

Figure 5 shows the H$_3$O$^+$ emission dynamics according to channel 3, which requires double hydrogen migration. It also involves the stabilization mechanisms mentioned above. From the AIMD simulation, we can identify two reaction pathways. The first case shown in Figure 5a starts with H$_2$ roaming, while the second one in Figure 5b starts with hydrogen transfer from C$_{\beta}$ to C$_{\alpha}$. Both reactions lead to the intermediate product CH$_3$CHOH$_2^+$, which is formed after around 150 fs for the H$_2$ roaming channel (Figure 5a) and after 90 fs for the hydrogen transfer channel (Figure 5b). Then both channels show a similar roaming of H$_2$O in the vicinity of C$_{\alpha}$ during which one hydrogen transfers from C$_{\beta}$ to C$_{\alpha}$. This transfer evolves on a rather flat PES (see Figure 5d) and results in long-time roaming of H$_2$O before it finally captures one proton from C$_{\alpha}$.

The analysis of the static PES shows two possible ways to form the intermediate CH$_3$CHOH$_2^+$: (i) hydrogen transfers from C$_{\alpha}$ to the hydroxyl group (see the red dashed line in Figure 5d),

\[
\text{CH}_3\text{CH}_2\text{OH}^+ \rightarrow \text{CH}_3\text{CHOH}_2^+ \tag{4}
\]

and (ii) hydrogen transfers from C$_{\alpha}$ to C$_{\beta}$ in the first step and then transfers from C$_{\alpha}$ to the hydroxyl group

\[
\text{CH}_3\text{CH}_2\text{OH}^+ \rightarrow \text{CH}_3\text{CHOH}^+ \rightarrow \text{CH}_3\text{CHOH}_2^+ \tag{5}
\]

In Figure 5c, the PESs of different isomers are shown as a function of the C$_{\alpha}$-O bond length, which eventually breaks for H$_3$O$^+$ emission. Without hydrogen transfer, the ethanol dication does not dissociate through C$_{\alpha}$-O bond breakage. As shown by the blue curve in Figure 5c, the PES of CH$_3$CH$_2$OH$^+$ as a function of the C$_{\alpha}$-O bond length shows a high potential barrier, which closes the dissociation channel. The isomeric transformation from CH$_3$CH$_2$OH$^+$ to CH$_3$CHOH$^+$ associated with a C$_{\alpha}$-O length increase only is also energetically forbidden due to the high potential energy barrier as marked by the red circle in Figure 5c. One possible pathway is expected, similar to that involved in C$_{\alpha}$-C$_{\beta}$ dissociation as shown in Figure 2f where a bond length increase is accompanied by hydrogen transfer. The energy level of such TS is marked by a red star in Figure 5c, which can be reached in the Franck-Condon region. Then the isomeric transformation from CH$_3$CHOH$^+$ to CH$_3$CHOH$_2^+$ occurs at their PES crossing point as shown by the left orange circle in Figure 5c. The relaxed PES scanning of the stable dication, i.e., CH$_3$CHOH$_2^+$, is shown by the orange curve in Figure 5c. With increasing C$_{\alpha}$-O bond length, one hydrogen from C$_{\beta}$ first transfers to C$_{\alpha}$ forming CH$_3$CHOH$_2^+$ and then transfers to oxygen emitting finally H$_2$O$^+$, as shown by the middle and right orange circles in Figure 5c. The associated TSs and their pathways are confirmed by the IRC calculations as shown in Figure 5d. The flat PES around TS-1 and TS-2 means that the double hydrogen migration has a relatively long lifetime before dissociation.

CONCLUSIONS

To summarize, the present study demonstrates for ethanol that the ultrafast PT can give rise to a competition between CE on the repulsive PES and isomerization and thereby influence the fragmentation pathway. Our molecular dynamics simulations and PES calculations show that hydrogen migration can stabilize the repulsive state of the ethanol dication before CE opening up new pathways. For the ethanol dication, there are three possible ways to stabilize the dication, i.e., hydrogen transfer from C$_{\alpha}$ to C$_{\beta}$ from carbon to hydroxyl, and the formation of intermediate H$_2$. All of the stabilization processes can take place within 25 fs, which is faster than CE.

It is worthwhile to note that the roaming trajectories can be far away from the IRC paths of the TSs, which can be seen by comparing the simulated trajectories and the IRC paths. This is the case in particular for the TS-3 in Figure 4g where a very high potential barrier is observed. The wide range roaming of H$_2$, as shown in Figure 4de, makes it possible to bypass the saddle point. The roaming chemistry also challenges the conventional TS theory in predicting KER of associated channels. As obtained in Figures 4fg and 5d, the energy difference between the highest energy level and the dissociation limit, which determines the KER, is always larger.
than the averaged KER of the experiment and AIMD results, which are shown in Figure 1d,e. This is due to the fact that the roaming process will lead to highly excited vibrational levels of final H$_2^+$ and H$_2$O$^+$. As a result, the KER of the experiment and AIMD is lower than that predicted by a static energy calculation.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c02074.

Additional information on experimental methods and computational methods (PDF)

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**Notes**

The authors declare no competing financial interest.

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