Photodissociation dynamics of benzoic acid

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The photodissociation of benzoic acid at 193 and 248 nm was investigated using multimass ion imaging techniques. Three dissociation channels were observed at 193 nm: (1) C₆H₅COOH → C₆H₅ + COOH, (2) C₆H₅COOH → C₆H₅CO + OH, and (3) C₆H₅COOH → C₆H₅ + CO₂. Only channels (2) and (3), were observed at 248 nm. Comparisons of the ion intensities and photofragment translational energy distributions with the potential energies obtained from ab initio calculations and the branching ratios obtained from the Rice–Ramsperger–Kassel–Marcus theory suggest that the dissociation occurs on many electronic states. © 2010 American Institute of Physics. [doi:10.1063/1.3274624]

I. INTRODUCTION

Photodissociation of carboxylic acids has been studied extensively due primarily to the generation of the OH radical and its relevance in atmospheric chemistry. Formic acid, HCOOH, the simplest of the organic acids, is the prototype in the series of carboxylic acid molecules. Previous investigations demonstrated five potential dissociation channels,

\[
\text{HCOOH} + \nu \rightarrow \text{HCO} + \text{OH}, \quad \Delta H = 108 \text{ kcal/mol}, \quad (1)
\]

\[
\rightarrow \text{H} + \text{HCOOH}, \quad \Delta H = 93 \text{ kcal/mol}, \quad (2)
\]

\[
\rightarrow \text{H} + \text{COOH}, \quad \Delta H = 103 \text{ kcal/mol}, \quad (3)
\]

\[
\rightarrow \text{H}_2 + \text{CO}_2, \quad \Delta H = 8.4 \text{ kcal/mol}, \quad (4)
\]

\[
\rightarrow \text{H}_2\text{O} + \text{CO}, \quad \Delta H = -1.4 \text{ kcal/mol}. \quad (5)
\]

These studies revealed that reactions (1) and (2) occur on the excited states and that reactions (3)–(5) result from the ground state. Near 220 nm the dominant process is OH formation via scission of the C—OH bond. At 222 nm, 70% of HCOOH molecules dissociate to yield OH radicals with the remaining 30% leading to C—H and O—H bond fissions and the production of H atoms. Large quantum yields for OH product were also found in the photodissociation of acetic acid (0.55–0.57) and propionic acid (0.15–0.35) at the same wavelength.

Kumar et al. studied the photodissociation of difluoroacetic acid. They found that decarboxylation [CO₂ elimination, analogous to reaction (4)] is important in thermal dissociation. On the other hand, OH products resulted solely from UV photodissociation. Butler and co-workers studied the photolysis of acrylic acid (H₂C==CHCOOH) monomers by at 193 nm light. Photofragment velocity distribution measurements indicate that C—C and C—O bond fissions are the major photodissociation pathways and that molecular de-carboxylation and decarboxylation reactions do not occur to a significant extent.

In addition to the molecules previously mentioned, a number of other (saturated and unsaturated) carboxylic acids have been examined, including pyruvic acid, thiolic acid, acrylic acid, propionic acid, and propynoic acid. The majority of these studies focused on the detection of the OH radical, not only because the OH radical is one of the important products but because this radical can be detected easily by laser induced fluorescence (LIF). One of the conclusions drawn from these studies is that these acids undergo dissociation to produce OH from an excited state featuring an exit barrier. However, the branching ratio for OH elimination along with other possible dissociation channels is not well understood for these compounds.

Benzoic acid is the simplest aromatic carboxylic acid. The production of OH from benzoic acid has been detected using LIF following excitation by ultraviolet (UV) photons. However, quantum yields for OH and other possible dissociation channels were not investigated. In our work, we report the photodissociation of benzoic acid in a molecular beam at 193 and 248 nm using multimass ion imaging techniques. In addition to the OH elimination channel, both CO₂ and COOH elimination channels were observed. Photofragment translational energy distributions are also reported. Comparisons with potential energies derived from ab initio calculations and branching ratios obtained from the Rice–Ramsperger–Kassel–Marcus (RRKM) calculations are made.

II. EXPERIMENT

The multimass ion imaging techniques we employ have been described in detail elsewhere along with information concerning the high-temperature nozzle we use. A brief description is provided here. A molecular beam containing benzoic acid is formed by flowing ultrapure Ne carrier gas at pressures of 250 Torr through a pulsed nozzle (coated with graphite). The nozzle is filled with a mixture of benzoic acid sample and graphite powder at 65 °C. Molecules in the

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molecular beam are irradiated by a UV laser beam (Lambda Physik, Compex 200: 20 ns pulse duration) and dissociated into neutral fragments. Due to recoil and center-of-mass velocities, the resulting fragments are distributed on an expanding sphere in flight to the ionization region. The fragments are subsequently ionized with a vacuum ultraviolet (VUV) (118 nm) laser pulse.

The distance and time delay between the VUV and photolysis laser pulses is set such that the VUV laser passes through the center of mass of the dissociation products and generates a line segment of photofragment ions by photoinitiation. The length of the segment is proportional to the fragment recoil velocity in the center-of-mass frame multiplied by the delay time between the photolysis and ionization laser pulses. To separate different masses within the ion segment, a pulsed electric field is used to extract the ions into a mass spectrometer after ionization. During mass analysis the length of each fragment ion segment continues to expand in the original direction according to its recoil velocity. At the exit port of the mass spectrometer, a two-dimensional (2D) ion detector is used to detect ion positions and intensity distributions. In this 2D detector, one direction represents the recoil velocity axis and the other direction the mass axis. The image of the ion intensity distribution for each mass-to-charge ratio generated from dissociation is a line-shape image.

Molecules not dissociated into fragments upon absorption of UV photons remain within the molecular beam. These molecules, which contain large internal energies, move at the molecular beam velocity to the ionization region where they are ionized by the VUV laser pulse. The wavelength of the VUV laser is set at 118.2 nm such that the photon energy is only sufficiently large to ionize parent molecules. The dissociation of parent molecular cations would not occur at energies remaining after VUV laser ionization. However, dissociation can occur following VUV laser ionization for those excited molecules, which had previously absorbed UV photons without having dissociated.

The image of the ion intensity distribution from dissociative ionization differs from the image resulting from the dissociation products of neutral parent molecules. Because ionization and dissociation occurred at the same position, the image of dissociative ionization was a 2D projection of the photofragment ion’s three-dimensional recoil velocity distribution. It was very similar to the image from conventional ion imaging techniques. It was a disklike image rather than a line-shape image. The size of the image from the dissociative ionization did not change with the delay time between the pump and probe laser pulses. Interestingly, the ionization of fragments possessing low ionization potentials or large internal energies resulted in dissociative ionization and generated smaller ionic fragments. Ion images from these reactions were disklike and the width changed with the delay time. From the shape of the image and its change in width with delay time, images from the dissociation of neutral molecules and the respective dissociative ionization of excited parent molecules and neutral fragments can be distinguished.

III. RESULTS

Fragments of mass-to-charge ratio $m/e=39, 45, 50, 52, 77, 78,$ and 105 were observed from the photodissociation of benzoic acid at 193 nm using a 118.2 nm photoionization laser beam. Figure 1 depicts the photofragment ion images. Fragments of $m/e=45, 77, 78,$ and 105 have line-shape images. The line-shape images suggest that the photofragments result from the dissociation of benzoic acid. The images of fragments $m/e=50$ and 52 are disklike. However, the widths of the disk change with the delay time. Instead of dissociative ionization from undissociated parent molecules, they must originate from the dissociative ionization of heavy fragments. From the widths of the disklike image, it can be determined that the photofragments are from the dissociative ionization of fragment C$_6$H$_6$. This is confirmed by our previous study, which found that benzene with a large amount of internal energy can be easily cracked into $m/e=50, 52,$ and 39 fragments upon VUV photoionization. The images suggest the following reactions:

$$C_6H_5COOH + h\nu(\text{UV})$$

$$\rightarrow C_6H_5(m=77) + COOH(m=45),$$

$$C_6H_5CO(m=105) + OH(m=17).$$

The intensity of fragment $m/e=39$ is very small. We only observed it in time of flight mass spectra. No image of $m/e=39$ was recorded. The VUV photon energy of 118.2 nm is 10.5 eV, which is smaller than the ionization energies of fragments, CO$_2$ and OH. As a result, we are unable to observe these two fragments. The photofragment translational distributions obtained from the images are illustrated in Fig. 2. The total fragment translational energy distributions obtained from heavy fragment C$_6$H$_5$ and from light fragment COOH match well with translational energies larger than 4 kcal/mol, confirming reaction (6). The distributions do not compare well with translational energies less than 4 kcal/mol. The intensity of fragment $m/e=77$ is larger than that of fragment $m/e=45$ in this region. This is partially due to the secondary dissociation of heavy fragment C$_6$H$_5$ [i.e., C$_6$H$_5H_2(m=78) \rightarrow C_6H_5(m=77) + H$] and partially due to the secondary dissociation of COOH with large internal energy.
Both secondary dissociations make the intensity of m/e=77 larger than that of m/e=45 in the lower translational energy region. Figure 2 also shows that the released translational energy is large for reaction (7). The maximum translational energy is as high as 80 kcal/mol. The large translational energy release is consistent with the potential energy from ab initio calculation (see below), which shows that the heat of reaction is small and the exit barrier height is large. On the other hand, the average translational energies released from reactions (6) and (8) are small. The small translational energies also agree with the potential energy from ab initio calculation (see below), which shows that the heat of reaction is large and there is no exit barrier for these two channels.

Table I summarizes the ratio of photofragment ion intensities. Branching ratios for the various reactions can be obtained from the normalization of these ion intensities by the ionization cross section for each fragment at this VUV wavelength (118.2 nm). Unfortunately, we do not have the ionization cross sections for these fragments at 118.2 nm. However, these ion intensities provide a rough estimate of the relative importance of these dissociation channels.

The photodissociation of benzoic acid at 248 nm was also investigated. Fragment ions of m/e=77, 78, and 105 were observed. The photofragment ion images are shown in Fig. 3. The image for m/e=77 is disklike and its width does not change with the delay time. It represents the dissociative ionization of the undissociated excited parent molecules. The ion images for m/e=78 and 105 are line shape. They result from reactions (7) and (8). The corresponding photofragment translational energy distributions are shown in Fig. 4.

### IV. DISCUSSION

The isomers of benzoic acid on the ground state, possible dissociation channels, and the relative positions of various electronic states from previous ab initio calculations are summarized in Fig. 5. There are two energy-minima structures for benzoic acid in the ground state. One has a planar structure and the other a nonplanar geometry in the COOH functional group. The first structure is more stable (relative energy of 6.6 kcal/mol). A barrier...
A few experimental and theoretical investigations have been adopted from Ref. 22. 

Room temperature absorption spectra show two absorption bands. One band from 290 to 260 nm with the maximum absorption at 273 nm (104.9 kcal/mol) and the other band from 260 nm to a wavelength shorter than 210 nm, with the maximum absorption at 220 nm (130.2 kcal/mol). In comparison with the calculation, they can be assigned to the excitation to the S_2 and S_3 states, respectively, although the calculated vertical excitation energy of the S_2 state is overestimated. No fluorescence was observed from the S_1 excited state. Benzoic acid in rigid glass (at 77 K) was found to show only phosphorescence and at a high quantum yield, indicating that an intersystem crossing to the lowest triplet state occurs very efficiently in benzoic acid. Sensitized phosphorescence excitation spectroscopy was used to observe the electronically excited states of benzoic acid in supersonic jets. Two sharp bands at 35 923 and 35 943 cm^{-1}, respectively, were assigned to the origins of the excitation from the ground state of two rotational isomers of benzoic acid to the S_1(1\pi\pi^*) excited state. Actually, they are S_1(1\pi\pi^*) instead of S_1(1\pi\pi^*) according to the previous ab initio calculation described in previous paragraph. Laser desorption followed by jet cooling has been utilized to identify the S_0→S_1 absorption spectrum of benzoic acid in the gas phase. The S_0→S_1 band origin was determined to be 35 960 cm^{-1} and the rate for intersystem crossing to the triplet state (as determined from the absorption linewidth) was found to be 1.2×10^{12} s^{-1}. These two experimental values of S_1 band origins are not very consistent and they are both higher than that from ab initio calculations.

Unlike that for the photodissociation of formic acid, only a few experimental and theoretical investigations have been performed on the photodissociation of benzoic acid. Early theoretical calculations showed that the energy of the transition state for decarboxylation [reaction (7)] is 62 kcal/mol. This energy falls to 31.5 kcal/mol for a benzoic acid-water complex. Recent theoretical calculations give the potential energy profiles for C—C and C—O bond fissions as well as decarboxylation from different electronic states, which are summarized in Fig. 5. The C—O bond cleavage leads to fragment products, C_6H_5CO and OH, in the ground state. This dissociation channel can occur on the ground state without an energy barrier or it can originate from the triplet T_2 state (with a barrier height of 102.3 kcal/mol). Nascent OH product state distributions from the photodissociation of benzoic acid have been measured using techniques employing LIF at different UV excitation wavelengths. By comparison of the OH product appearance threshold obtained from experimental measurement and the dissociation thresholds of various electronic states from calculations, the T_2 state is proposed to be the dissociative state for OH elimination channel. The same theoretical calculations show that the heat of reaction to generate fragments, C_6H_5CO and COOH, in the ground state is 109 kcal/mol. It can occur from the triplet state (with a barrier of 121 kcal/mol) or from the ground state (without an energy barrier).

We also performed ab initio methods to calculate geometries and energies of various isomers, transition states, and dissociation products in the ground electronic state. In the calculations, the geometries were optimized at the hybrid density functional B3LYP/6-31G level and the energies were calculated using the G3 model chemistry scheme. The results for various dissociation channels are summarized in Figs. 6 and 7. Hydrogen atom elimination from various molecular positions is energetically possible dissociation channels. Dissociation thresholds for C—H bond cleavage in aromatic rings are in the range of 113.9–117.4 kcal/mol, depending on the position of the C—H bond. These thresholds are all close to the 248 nm photon energy. The elimination of hydrogen from OH requires less energy than does C—H bond fission from the aromatic ring. These H atom elimination channels do not have an exit barrier, as shown in Fig. 6. The barrier height for the secondary dissociation C_6H_5COO (after O—H bond fission) to C_6H_5+CO_2 is as large as 119 kcal/mol. It only becomes possible at 193 nm. The threshold
for OH elimination is only 106.8 kcal/mol. Secondary dissociation following OH elimination to produce C₆H₅+CO has a large barrier height (131.8 kcal/mol) and a large heat of reaction. On other hand, COOH elimination has a relatively low threshold (108.2 kcal/mol). The pathways of other dissociation channels, including CO, H₂O, and CO₂ eliminations, are shown in Fig. 7. They are all energetically allowed at both 248 and 193 nm. For CO elimination, the channel producing C₆H₅O fragments has a barrier height of 87.2 kcal/mol, the other CO elimination channel, which produces a C₆H₅OH fragment, has a barrier height of 95.2 kcal/mol. Water elimination also has two pathways. One has a very high barrier (112 kcal/mol) as well as a large heat of reaction (109.8 kcal/mol). These values are close to the 248 nm photon energy. Therefore, it is not likely to occur at 248 nm. The barrier height and heat of reaction of the other water elimination pathway are only 81.4 and 73.1 kcal/mol, respectively. It can occur at both photolysis wavelengths. Compared to CO and H₂O elimination, CO₂ elimination has a very low barrier height (71 kcal/mol). Our RRKM calculations on the electronic ground state find that CO₂ elimination is the dominant channel. The relative branching ratios are 90% and 10% for the CO₂ and H₂O elimination channels at 193 nm. They become 65% and 35% at 248 nm.

Our experimental results reveal that OH elimination channel is important at 248 nm. This is consistent with the previous study. However, our results find that CO₂ elimination is also important at this wavelength. Since our RRKM calculation suggests that the branching ratio of OH elimination on the ground state is very small, this channel must occur on the excited state. On the other hand, RRKM calculation also predicts that CO₂ and H₂O elimination channels are both important for the dissociation occurring on the ground state at this wavelength. Since we do not observe the products corresponding to H₂O elimination, therefore, it is not likely that CO₂ elimination occurs on the ground state. As the photolysis wavelength changes from 248 to 193 nm, OH elimination becomes less important. The major channels are CO₂ and COOH elimination. Because RRKM calculations point to CO₂ elimination as the dominant channel on the ground state at 193 nm, the observation of large ion intensities for m/e=77 (C₆H₅) and m/e=45 (COOH) suggests that COOH elimination does not occur on the ground state. According to previous calculations the possible excited states for OH and COOH elimination are T₂ and T₁ state, respectively.

In summary, we find that many electronic states are involved in the photodissociation processes of benzoic acid. At this moment, we do not have clear evidence to identify the electronic state for each dissociation channel. On the other hand, the experimental observation shows that the dissociation properties of benzoic acid at 248 nm are quite similar to those for other carboxylic acids, i.e., elimination of OH is the major channel. However, the photodissociation properties at 193 nm show significant differences from that of most of the carboxylic acids studied at longer wavelengths. The minor channel is OH elimination and the major channels are CO₂ and COOH elimination.