Photodissociation of ethylbenzene and \( n \)-propylbenzene in a molecular beam

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The photodissociation of jet-cooled ethylbenzene and \( n \)-propylbenzene at both 193 and 248 nm was studied using vacuum ultraviolet photoionization/multimass ion imaging techniques. The photofragment translational energy distributions from both the molecules obtained at 193 nm show that the probability of portioning energy to product translational energy decreases monotonically with increasing translational energy. They indicate that the dissociation occurs from the ground electronic state. However, the photofragment translational energy distributions from both molecules obtained at 248 nm contain a fast and a slow component. 75% of ethylbenzene and 80% of \( n \)-propylbenzene following the 248 nm photoexcitation dissociate from electronic excited state, resulting in the fast component. The remaining 25% of ethylbenzene and 20% of \( n \)-propylbenzene dissociate through the ground electronic state, giving rise to the slow component. A comparison with an \textit{ab initio} calculation suggests that the dissociation from the first triplet state corresponds to the fast component in translational energy distribution. © 2002 American Institute of Physics. [DOI: 10.1063/1.1507117]

I. INTRODUCTION

The absorption of benzene and alkyl-substituted benzenes in the 190–270 nm region corresponds to the excitation of the phenyl ring. The excitation of the phenyl ring results in an excited state which is stable with respect to dissociation. The dissociation must occur indirectly either through the coupling between the stable and repulsive states, or after internal conversion from an initially excited state to a lower electronic state. The photodissociation mechanism has been postulated to be predissociation.\(^1\) However, the measurements of fragment formation rates and the transient absorption spectrum following the ultraviolet (UV) excitation suggested that highly vibrationally excited molecules are produced in the UV photodissociation of benzene and alkylbenzene.\(^2\)–\(^15\) A vibrationally hot molecule is produced by an internal conversion from the electronically excited state, which is populated by UV absorption. Intramolecular vibrational energy redistribution (IVR) occurs rapidly before the dissociation from the initially prepared (by internal conversion) highly vibrationally excited molecule. The extensive energy randomization among the vibrational degrees of freedom results in a slow dissociation rate and limited energy released to the product recoil kinetic energy (assuming that the exit barrier is small).\(^1\) The dissociation rates and photo-fragment translational energy distribution of hot molecules usually can be described by statistical theories. Compared to the dissociation of vibrationally hot molecules on the ground electronic state with a small exit barrier, dissociation from the electronic excited state is usually fast, and the energy release in kinetic energy is often large.

The photophysics and photochemistry of benzene and toluene in the first and the second singlet excited states have been studied extensively.\(^3\)–\(^6\),\(^9\)–\(^12\),\(^16\) The fast relaxation from the \( S_2 \) and \( S_1 \) states to the \( S_0 \) state, the slow dissociation rates, and the small amount of energy released to the photofragment translational degrees of freedom support the conclusion that the mechanism is via internal conversion to the ground electronic state. In contrast to benzene and toluene, prior experimental measurements of the other alkylbenzenes were limited to the dissociation rates and product branching ratios. For the photodissociation of ethylbenzene at 193 nm (\( S_2 \) state), the dominant channel is the C–C bond cleavage. A CH\(_3\) yield of 96±4% and a dissociation rate of 2\( \times 10^7 \) s\(^{-1} \) were reported.\(^4\)–\(^7\),\(^10\) The dissociation channel due to the H atom elimination was also observed.\(^7\) Ethyl radical elimination was found to be the major channel for the photodissociation of \( n \)-propylbenzene at 193 nm, and the dissociation rate is 7\( \times 10^6 \) s\(^{-1} \).\(^15\) A dissociation mechanism through internal conversion to \( S_0 \) was used to interpret the dissociation rates and branching ratios of xylene, ethylbenzene, \( n \)-propylbenzene, isopropylbenzene, butylbenzene, and trim...
ethylbenzene at 193 and 157 nm. No dissociation experiment has been performed for these molecules in the $S_1$ state. However, the onset and ultimate dominance of IVR in these molecules as the alkane chain is increased was found in the single vibronic level fluorescence spectra of the $S_1$ state. More recent high resolution laser fluorescence excitation spectra near the band origin of the $S_1$ state showed that propylbenzene and butylbenzene exhibit the excess linewidth, but the source of the excess width remains elusive.

In the previous study, we demonstrated that the photofragment translational energy distribution of ethylbenzene obtained at 248 nm ($S_1$ state) contains two components. It indicates some of the ethylbenzene molecules dissociate through the electronic excited state. In this work, we extend the study to ethylbenzene, $d_{10}$-ethylbenzene, and $n$-propylbenzene at both 193 nm and 248 nm. Photofragment translational energy distributions at 193 and 248 nm were measured using vacuum ultraviolet (VUV) photoionization/multimass ion imaging techniques. The results were interpreted by considering the potential energy surfaces of electronic ground state and the first triplet state obtained from an ab initio calculation.

II. EXPERIMENT

The experiments have been described in detail elsewhere, and only a brief description is given here. Ethylbenzene or $n$-propylbenzene vapor was formed by flowing ultrapure Ar at pressures of 300 Torr through a reservoir filled with liquid sample at 15 °C. The ethylbenzene (or propylbenzene)/Ar mixture was then expanded through a 500 μm high temperature (110 °C) pulsed nozzle to form the molecular beam. Molecules in the molecular beam were photodissociated by an UV photolysis laser pulse (Lambda Physik Compex205, ~20 ns). Due to the recoil velocity and center-of-mass velocity, the fragments were expanded to a larger sphere on their flight to the VUV laser beam, and then ionized by a VUV laser pulse. The distance and time delay between the VUV laser pulse and the photolysis laser pulse were set such that the VUV laser beam passed through the center-of-mass of the dissociation products, and generated a line segment of photofragment ions through the center-of-mass of the dissociation products by photoionization. The length of the segment was proportional to the fragment recoil velocity in the center-of-mass frame multiplied by the delay time between the photolysis and the ionization laser pulses. To separate the different masses within the ion segment, a pulsed electric field was used to extract the ions into a mass spectrometer after ionization. While the mass analysis was being executed in the mass spectrometer, the length of each fragment ion segment continued to expand in the original direction according to its recoil velocity. At the exit port of the mass spectrometer, a two-dimensional ion detector was used to detect the ion positions and intensity distribution. In this two-dimensional detector, one direction was the recoil velocity axis and the other was the mass axis. The schematic diagram of the experimental set up is shown in Fig. 1.

According to the velocity of the molecular beam, it was necessary to change the distance between the photolysis laser beam and the VUV laser beam to match the delay time between these two laser pulses to ensure that the ionization laser would pass through the center-of-mass of the products. The change of the distance between the two laser beams changed the length of the fragment ion segment in the image. The relationship between the length of the ion image and the position of the photolysis laser is illustrated in Fig. 2. If the molecules were not dissociated after the absorption of UV photons, these high internal energy molecules would remain within the molecular beam. They flew with the same velocity (molecular beam velocity) to the ionization region and were ionized by the VUV laser. The wavelength of the VUV laser in this experiment was set at 118.2 nm such that the photon energy was only large enough to ionize parent molecules. The dissociation of parent molecule cations would not occur.

FIG. 1. Schematic diagram of the multimass ion imaging detection system. (1) nozzle; (2) molecular beam; (3) photolysis laser beam; (4) VUV laser beam, which is perpendicular to the plane of this figure; (5) ion extraction plates; (6) energy analyzer; (7), (8), and (9) simulation ion trajectories of $m/e$ = 16, 14, 12; (10) two-dimensional detector, where the Y-axis is the mass axis, and the X-axis (perpendicular to the plane of this figure) is the velocity axis.

FIG. 2. The relation between the lengths of the image result from different photolysis laser positions and the disk-like image from the dissociation after ionization. (1) represents the crossing point of the molecular beam and the VUV laser beam, where the dissociative ionization occurs. (2) and (3) represent the lengths of the fragment ion segment created by the VUV laser photoionization from two different photolysis laser positions. (4) and (5) represent the lengths of the fragment ion on the detector from two different photolysis laser positions. (6) encircles the region of the disk-like image. $t_1$ and $t_2$ represent the two different delay times between the photolysis laser pulse and the VUV laser pulse. $\Delta t$ is the flight time in the mass spectrometer.
with the energy left after the VUV laser ionization. However, the dissociation occurred following the VUV laser ionization for those hot molecules, which absorbed UV photon without dissociation. The ion image of the dissociative ionization was different from the image due to the dissociation products of neutral parent molecules. Since ionization and dissociation occurred at the same position, the image of dissociative ionization was a 2-D projection of the photofragment ion's 3-D-recoil velocity distribution. It was very similar to the image from the conventional ion imaging techniques and was a disk-like image, rather than a line-shape image. From the shape of the image and its change with the delay time, the image from dissociation of neutral molecules can easily be distinguished from the dissociative ionization image.

The dissociation rate can be obtained from the product growth with respect to the delay time between the pump and probe lasers. However, an accurate measurement can be obtained only when the dissociation rate is fast enough before the parent molecules and fragments fly out of the detection region due to the molecular beam velocity and recoil velocity, respectively. Another approach is to measure the disappearance rate of the parent molecules, that is, the intensity change of the disk-like images at various delay times along the molecular beam. In addition to these methods, the dissociation rate can also be obtained from the line-shape image intensity distribution. Since the intensity of the line-shape image results from the accumulation of the products produced during the time period from the pump pulse to the probe pulse, the ion image intensity distribution is a function of both the fragment recoil velocity distribution and the dissociation rate. Therefore, the velocity distribution and the dissociation rate can be obtained from the image. The simulation in Fig. 3 shows the effect of the dissociation rate on the ion image intensity distribution. For a given fragment recoil velocity distribution, as shown in Fig. 3(a) for a large recoil velocity distribution and Fig. 3(d) for a small velocity distribution, the image intensity distributions from a fast dissociation rate, as illustrated in Figs. 3(b) and 3(e), are different from that of a slow dissociation rate, as presented in Figs. 3(c) and 3(f). The advantage of the measurement from the images is the following. If the fragment image contains more than one component (either disk-like images or multi-components in the line-shape image), the dissociation rates and velocity distributions of each component can be determined separately. This avoids the fit of the experimental data obtained from the product growth or the parent decay to the multi-exponential functions in a low signal to noise ratio situation. In this work, the dissociation rates were obtained from the product growth when the dissociation rate is fast enough before the parent molecules and fragments fly out of the probe region. On the other hand, dissociation rates were obtained from the disk-like image intensity decay for slow dissociation rate and from the line-shape image intensity simulation for multi-component dissociation channels.

III. RESULTS

A. Photodissociation at 193 nm

Figure 4(a) depicts the photofragment ion images obtained from the photodissociation of ethylbenzene at 193 nm. Fragments of \( m/e = 91, 92 \) and 93 correspond to the phenyl radical and its \(^{13}\)C isotopes due the natural abundance. The fragment translational energy distribution obtained from the ion image is presented in Fig. 4(b). The monotonic decrease of the probability with the increasing translational energy is the characteristic of dissociation from a molecule undergo internal conversion to the ground electronic state with no exit barrier. The similar phenomenon was also observed in the photodissociation of \( d_{10} \)-ethylbenzene and n-propylbenzene, as shown in Fig. 5 and Fig. 6.

B. Photodissociation at 248 nm

The photofragment ion images of ethylbenzene obtained at 248 nm are significantly different from those obtained at 193 nm. Figures 7(a) and 7(b) illustrate the ion images of phenyl radicals obtained from the photodissociation of ethylbenzene at 248 nm at two different delay times. It clearly shows that the image of fragment \( m/e = 91 \) has three components. A component located on both wings and a line-shape component superimposed on a disk-like component at the center. As the delay time between the pump and the probe laser pulses increased, the component on both wings moved rapidly toward the outside, and the length of the line-shape component at the center increased. On the other hand, the size of the disk-like image did not change, but the intensity decreased with the increase of the delay time. These three components can be assigned easily according to the relationship illustrated in Fig. 2. The component on the wings and the line-shape component are the phenyl radical fragments...
that resulted from the dissociation of ethylbenzene with large recoil velocity and small recoil velocity, respectively. The third component, the disk-like image, was from the dissociative ionization of undissociated hot ethylbenzene by VUV photoionization due to the slow dissociation rate at 248 nm. Among these three components, the decay rate of the disk-like component was found to be $1.1 \times 10^5$ s$^{-1}$, as illustrated in Fig. 7c. The product growth rates of the phenyl radical with large recoil velocity and small recoil velocity components were obtained by forward convolution simulation from the images at various delay times. It shows that the product growth rate of the large recoil velocity component is faster than $1 \times 10^6$ s$^{-1}$, and that of the small velocity component is $1 \times 10^5$ s$^{-1}$. The photofragment translational energy distribution obtained from the line-shape ion image by forward convolution is shown in Fig. 7d. The different dissociation rates suggest that there are two mechanisms involved in the dissociation of ethylbenzene at 248 nm. For the component of small recoil velocity, the average translational energy release is small and the dissociation rate is slow. These are the characteristics of dissociation from the ground electronic state. In contrast, the dissociation rate for the component of large recoil velocity is fast, the average released translational energy is large, and the peak of the distribution is located at 18 kcal/mol. These are the characteristics of dissociation from a repulsive excited state, or dissociation from an electronic state with an exit barrier.

The similar results were obtained for the photodissocia-

- tion of $d_{10}$-ethylbenzene and $n$-propylbenzene, as illustrated in Figs. 8–11. For $n$-propylbenzene, the intensity decay rate of the disk-like image was found to be $4.9 \times 10^4$ s$^{-1}$, and the product growth rates obtained from simulation are $5 \times 10^4$ s$^{-1}$ and larger than $5 \times 10^5$ s$^{-1}$ for the slow velocity component and the fast recoil velocity component, respectively.

A photolysis laser fluence dependence measurement was carried out in the region of 0.7 mJ/cm$^2$ to 10 mJ/cm$^2$ for 193 nm and 2.2 mJ/cm$^2$ to 33 mJ/cm$^2$ for 248 nm. The shapes and the ratio of these two components in the translational energy distribution do not change with photolysis laser inten-

![FIG. 4. (a) Ion image of photofragments from the photodissociation of ethylbenzene at 193 nm. The total delay time between the pump laser and probe laser pulses is 22 µs. Fragment $m/e=92$ is the $^{13}$C isotope of fragment $m/e=91$, and $m/e=90$ and 89 result from two-photon dissociation. (b) The fragment translational energy distribution for the reaction $C_6H_5C_2D_5-C_6H_5CD_2+CH_3$. The arrow indicates the maximum available energy from one-photon dissociation.](image1)

![FIG. 5. Ion image of photofragments (a) $m/e=98$, (b) $m/e=18$ from photodissociation of $d_{10}$-ethylbenzene at 193 nm. The delay times between pump and probe laser pulses are 30 µs and 7 µs, respectively. (c) The translational momentum distributions of $m/e=18$ (thin solid line) and 98 (thick solid line). (d) The fragment translational energy distribution for the reaction $C_6D_5C_2D_5-C_6D_5CD_2+CD_3$.](image2)

![FIG. 6. Ion image of photofragments (a) $m/e=91$, (b) 29 from photodissociation of $n$-propylbenzene at 193 nm. The delay times between pump and probe laser pulses are 28 µs and 8 µs, respectively. (c) The translational momentum distributions of $m/e=29$ (thin solid line) and 91 (thick solid line). (d) The fragment translational energy distribution for the reaction $C_6H_5C_3H_7-C_6H_5CH_2+CH_3$.](image3)
sity and the maximum translational energies are less than the available energies from one-photon dissociation. The measurements suggest that they all result from one-photon dissociation.

IV. DISCUSSIONS

Since the ethyl and propyl groups are not the electronic chromophore at 248 nm, the photon absorption corresponds to the excitation of the phenyl ring. Dissociation must occur indirectly either through the coupling between the stable and repulsive states, or after the internal conversion from the initial excited state to a lower electronic state. Figure 12 shows the potential energy diagram of the reaction \( \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \). In the ground electronic state, the methyl group changes gradually from pyramidal geometry to planar geometry as the C–C bond length increases during the dissociation process. There is no exit barrier for the dissociation from the ground state. This indicates that the slow component in the translational energy distribution results from the ground state dissociation and the fast component did not result from the ground state dissociation. The fast component must result from either through the coupling between the stable and repulsive states, or a lower electronic state with an exit barrier. Figure 12 also shows the potential energy diagram in the first triplet state for the same dissociation channel. The exit barrier height is about 31 kcal/mol. Similar potential energy diagrams were found in the photodissociation channel of \( n \)-propylbenzene; the corresponding calculated energies for \( n \)-propylbenzene are shown in parentheses in Fig. 12. The dissociation from the ground state is barrierless. However, the dissociation from the first triplet state has a barrier height of 32 kcal/mol. Although the other electronic states cannot be definitively excluded (no potential energy surfaces for the other excited states are available), the

![Velocity axis](image1)

FIG. 7. The ion image of a phenyl radical obtained from the photodissociation of ethylbenzene at 248 nm at two different delay times: (a) 15 \( \mu \)s, (b) 32 \( \mu \)s. (c) Intensity decay of the disk-like image as a function of delay times. A decay rate of \( 10^5 \) s\(^{-1} \) was obtained. (d) The fragment translational energy distribution for the reaction \( \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \). The arrow indicates the maximum available energy from one-photon dissociation.

![Velocity axis](image2)

FIG. 8. The fragment ion image obtained from the photodissociation of \( d_{10} \)-ethylbenzene at 248 nm. (a) \( m/e = 98 \), delay time 30 \( \mu \)s; (b) \( m/e = 18 \), delay time 7 \( \mu \)s.

![Velocity axis](image3)

FIG. 9. (a) The translational momentum distributions of \( m/e = 18 \) (thin solid line) and 98 (thick solid line). (b) The fragment translational energy distribution for the reaction \( \text{C}_6\text{D}_5\text{C}_2\text{D}_5 \rightarrow \text{C}_6\text{D}_5\text{CD}_2\text{CD}_3 \).

![Velocity axis](image4)

FIG. 10. Ion image of photofragment (a) \( m/e = 91 \), (b) 29 from photodissociation of propylbenzene at 248 nm. The delay times between pump and probe laser pulses are 20 \( \mu \)s and 5 \( \mu \)s, respectively. The image of \( m/e = 30 \) is the mass indicator.
exit barrier in the first triplet state and the translational energy distribution of the fast component in both ethylbenzene and propylbenzene suggest that dissociation upon intersystem crossing to the first triplet state is a likely explanation for the fast component in the translational energy distribution of ethylbenzene and n-propylbenzene.

Two-color photoionization has been applied to the measurement of the time evolution of laser excited first singlet state of benzene, toluene, ethylbenzene, and xylene. The observed photoionization signals exhibited a biexponential dependence upon the time delay between the pump and ionization lasers. The fast exponential decay resulted from the relaxation of the $S_1$ state, and the slow exponential decay was interpreted as the decay of the $T_1$ state after the $S_1 \rightarrow T_1$ intersystem crossing. Although the triplet state was found to play an important role in the relaxation of the $S_1$ state in those molecules, the interpretation of the $T_1$ state decay was only attributed to the intersystem crossing from the $T_1$ state to the $S_0$ state. No dissociation from the $T_1$ state following the excitation of the first singlet state has been reported. In those studies, the decay rates were monitored as a function of vibrational energy and were found to increase with energy. For ethylbenzene, the decay rate of the triplet state was found to be $4 \times 10^4$ s$^{-1}$ at the excitation wavelength of 266 nm. In this work, the excitation energy is larger than the energy in the previous study, and the increase of the decay rate, therefore, is expected. However, additional channels may open as the energy increases and result in the competition with the intersystem crossing from the $T_1$ state to the $S_0$ state. Our experimental results demonstrate that the dissociation not only competes with the intersystem crossing but also becomes the dominant channel at the excitation wavelength of 248 nm.

In conclusion, the fragment translational energy distribution and dissociation rate measurements of ethylbenzene and n-propylbenzene suggest that the dissociation mechanisms at 193 and 248 nm are different. For ethylbenzene and n-propylbenzene, molecules following 193 nm excitation dissociate through the hot molecule mechanism. It indicates that the coupling between the $S_2$ and $S_0$ states, or the coupling between the $S_2$ and $S_0$ states through some intermediate states, is very strong at this energy level. As a result, ethylbenzene and n-propylbenzene excited by a 193 nm photon converts to ground electronic state prior to dissociation. On the other hand, most of the ethylbenzene and n-propylbenzene following 248 nm excitation dissociate from the first triplet state. The dissociation of ethylbenzene and n-propylbenzene from the $S_0$ state could result from the directly internal conversion $S_1 \rightarrow S_0$, or through the two-step intersystem crossing $S_1 \rightarrow T_1 \rightarrow S_0$. Therefore, the minimum values of 0.75 and 0.8 for the intersystem crossing quantum yield of ethylbenzene and propylbenzene, respectively, can be determined from the ratio of the fast and slow components in the translational energy distribution. The high intersystem crossing quantum yield indicates the strong coupling between the $S_1$ and $T_1$ states at this energy level. The results suggest that dissociation from the first triplet state may play a very important role in the photoexcitation of alkylbenzenes in the $S_1$ state.

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