Photoisomerization and Photodissociation of Aniline and 4-Methylpyridine

Chien-Ming Tseng,† Yuri A. Dyakov,† Cheng-Liang Huang,†,‡ Alexander M. Mebel,†,§ Sheng Hsien Lin,†,†† Yuan T. Lee,†,† and Chi-Kung N*†

Contribution from the Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23–166, Taipei, Taiwan and Chemistry Department, National Taiwan University, Taipei, Taiwan

Received March 21, 2004; E-mail: ckni@po.iams.sinica.edu.tw

Abstract: Photoisomerization and photodissociation of aniline and 4-methylpyridine at 193 nm were studied separately using multimass ion imaging techniques. Photofragment translational energy distributions and dissociation rates were measured. Our results demonstrate that more than 23% of the ground electronic state aniline and 10% of 4-methylpyridine produced from the excitation by 193 nm photons after internal conversion isomerize to seven-membered ring isomers, followed by the H atom migration in the seven-membered ring, and then rearomatize to both methylpyridine and aniline prior to dissociation. The significance of this isomerization is that the carbon, nitrogen, and hydrogen atoms belonging to the alkyl or amino groups are involved in the exchange with those atoms in the aromatic ring during the isomerization.

I. Introduction

Today, aromatic photochemistry is a major area of study. The conspicuous feature that has emerged from the studies of aromatic photochemistry is that the photoexcitation of the benzene ring leads to a rich variety of reactions. The UV fluorescence quantum yields of aromatic molecules in the S_1 state decrease rapidly with the increase of photon energy. For these molecules, the most important monomolecular processes after excitation to the S_1 state is photoisomerization with their further rearomatization. It has been suggested that this kind of isomerization proceeds by the intermediary formation of isomers such as benzvalene and prismane, as well as isomerization with a change of the alkyl substitute’s position in the aromatic ring. The generally accepted view is that photoisomerization of this kind proceeds by the intermediary formation of isomers such as benzvalene and prismane with their further rearomatization. It has been suggested that all isomerization processes of benzene and its alkyl derivatives can be described in terms of ring permutation. The ring permutation has been observed in benzene and alkyl-substituted benzene in the condensed phase and in the gas phase after the excitation to the S_1 state. The similar ring permutation were also used to describe the isomerization of nitrogen contained heterocyclic aromatic molecules. Recently, different isomerization mechanisms have been suggested, which involves the ring closure, followed by nitrogen migration around the sides of the cycloheptenyl ring, and then rearomatization. One important characteristic of both the ring permutation and ring closure mechanisms is that the carbon (or nitrogen) and hydrogen atoms belonging to the alkyl groups (or amino group) are not involved in the exchange with those atoms in the aromatic ring.

As the photon energy increases, the rate of internal conversion increases rapidly. Internal conversions of benzene and its derivatives are known to take place in subpicosecond time scale for the S_2 state. Most of these molecules in the S_2 state undergo internal conversion to the ground electronic state and become highly vibrational excited, or “hot molecule”. Since the energy of the S_2 state is much larger than the bond energy, dissociation is expected to occur. However, because of the sharing of internal

1 Institute of Atomic and Molecular Sciences, Academia Sinica.
2 Present address: Department of Applied Chemistry, National Chiayi University, Chiayi, Taiwan.
3 Present Address: Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199.
4 Chemistry Department, National Taiwan University.
energy among a large number of vibrational degrees of freedom in the hot molecules, the dissociation of a hot molecule is a rather slow process. For example, for a benzene molecule with the internal energy of 146 kcal/mol which is far exceeding the C–H bond dissociation energy of 110 kcal/mol, the average dissociation lifetime is as long as 10 μs.\(^{21}\) One of the very interesting aspects of benzene and its derivatives is the fact that below the bond dissociation energy, there are many structural isomers and the activation energy for isomerization also lies below the bond dissociation energy. Consequently, isomerization processes are expected to take place before a molecule finds its way to dissociate.

More recently, we observed a small amount of CD\(_3\)H, CD\(_2\)H, and CH\(_3\) and their heavy fragment partners, C\(_6\)H\(_4\)D, C\(_6\)H\(_3\)D\(_2\), C\(_6\)H\(_2\)D\(_3\), from the dissociation of isotope-labeled toluene, C\(_6\)H\(_4\)(CD\(_3\)), after the excitation to the S\(_2\) state.\(^{22}\) It clearly indicates that direct C–H bond and C–C bond cleavages in the electronic state are not the only dissociation mechanism. Another dissociation channel must exist, which allows for the exchange of D atoms in the methyl group with H atoms in the aromatic ring prior to dissociation. In addition, the small amount of CH\(_3\) resulting from C\(_6\)H\(_4\)\(^{13}\)CH\(_3\) dissociation suggests that not only are hydrogen atoms involved in the scrambling, but also that carbon atoms in both the methyl group and the aromatic group are involved in the exchange. The result was interpreted as the isomerization from six-membered ring to seven-membered ring (cycloheptatriene), followed by H atom migration within seven-membered ring molecule, and then rearomatization prior to dissociation.\(^{22}\) Similar isomerization was also observed in the photodissociation of xylene.\(^{23}\) The significance of this isomerization is that it is totally different from the ring permutation, since the carbon atoms and hydrogen atoms belonging to the alkyl group are not involved in the exchange with those atoms in the aromatic ring during the ring permutation.

However, this particular isomerization in alkyl-substituted benzenes can only be observed using isotope-labeled compounds. For nonisotope-labeled molecules, the effect of this isomerization is equivalent to that of ring permutation. For example, the consequence of xylene through this isomerization is the exchange of relative alkyl group positions, which gives practically the same result as the ring permutation. On the other hand, if this isomerization is open for heterocyclic aromatic molecules, then it is not necessary to have isotope-labeled compounds and one can easily change the chemical function groups during the process. For instance, methylpyridine can be changed to aniline through this isomerization.

In this work, we extend the study to photoisomerization of aniline and 4-methylpyridine. The results suggest that the isomerization from six-membered ring to seven-membered ring after internal conversion also plays a very important role in nitrogen atom contained aromatic molecules. A comparison of 4-methylpyridine and aniline with potential energy from ab initio calculation and toluene has been made.


**II. Experiment**

The experimental techniques have been described in detail in our previous reports on other aromatic molecules,\(^{24,25}\) and only a brief description is given here. Aniline or 4-methylpyridine vapor was formed by flowing ultrapure He (or Ne) at pressures of 500 Torr through a reservoir filled with liquid sample at 20 °C. The aniline/He or 4-methylpyridine/He mixture was then expanded through a 500 μm pulsed nozzle at 50 °C to form a molecular beam. Molecules in the molecular beam were photodissociated by a 193 nm laser pulse. Due to the recoil velocity and center-of-mass velocity, the fragments were expanded to a larger sphere on their flight to the ionization region, and then ionized by a VUV laser pulse. The VUV wavelength we used was 118.2 nm. 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 identification of the dissociation products and the measurement of their translational energy distributions were therefore simultaneously obtained from the image. The schematic diagram of the experimental set up is shown in Figure 1.

The dissociation rates were obtained from the product growths or the decay of parent molecules with respect to the delay time between the pump and probe lasers using time-of-flight mass spectrometer. However, accurate measurement can be achieved 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.

Aniline (99.8%), \(d_5\)-aniline (99%), and 4-methylpyridine (99%) were purchased from Acros Organics. \(d_3\)-4-methylpyridine (98%) was from Aldrich. These chemicals were used directly without further purification. The amounts of impurities were checked by both TOF mass spectrum and NMR spectroscopy. Mass spectrum shows that the total ion intensity of \(m/e\) values other than that of parent molecule is less than 1% in both aniline and 4-methylpyridine. In addition, NMR spectroscopy shows that no 4-methylpyridine can be detected in aniline, and no aniline can be detected in the 4-methylpyridine (less than 0.3% according to the S/N ratio of the spectrum).

III. Results

Aniline. Figure 2 shows the photofragment ion images of aniline. Fragments of \(m/e = 92, 91, 78, 77, 76, 17,\) and 15 were observed. The study of photolysis laser power dependence in the region of 1.2–10 mJ/cm\(^2\) showed that \(m/e = 90\) was due to the two photon dissociation and all the other fragments were from one-photon dissociation. Fragments resulted from multiphoton dissociation will not be discussed in this work.

Images of \(m/e = 92, 91, 77,\) and 76 represent four major dissociation channels of aniline, i.e., H, \(H_2\), \(NH_2\), and \(NH_3\) eliminations, respectively. Some of the light fragment partners with ionization potentials lower than the VUV photon energy were observed, as presented in Figure 2a. In addition, the image intensity of \(m/e = 78\) is 2.8 times larger than that of \(^{13}\)C isotope of \(m/e = 77\), indicating the existence of fragment \(^{13}\)C\(_3\)NH\(_4\). It corresponds to the minor dissociation channel of \(CH_3\) elimination. This channel can be further confirmed by the observation...
of its light fragment partner CH$_3$, as shown in Figure 2a. The momentum matches between the heavy and light fragment partners also exclude the contribution from three-body dissociation, like the dissociation of clusters, or the contribution from cation dissociation. Some fragments corresponding to the ring-opening dissociation channel like $m/e = 66, 54, 53, 52, 41, 40, 39$ were also observed. However, they were all very small and will not be discussed in this work.

Photofragment translational energy distributions obtained from the image are illustrated in Figure 3. Translation energy distribution of H atom elimination shows two components. The ratio between the fast and slow components is about 3:1. For the slow component, the average translational energy release is small and the probability of fragment translational energy distribution decreases monotonically with the increase of energy. These are the typical characteristics of the dissociation from hot molecules. On the other hand, the average released translational energy for the fast component is large, and the peak of the distribution is located at 24 kcal/mol. It must result from a repulsive state, or a state with a large exit barrier. Image intensity profiles of $m/e = 92$ at the photolysis laser polarization parallel and perpendicular to the VUV laser beam are shown in Figure 4. They have the same shape and intensity, indicating the isotropic fragment distribution of both the slow and fast H atom components.

Two-component translational energy distribution was also observed in H$_2$ elimination channel. The ratio between the fast and slow components is about 10:1. For the NH$_3$, CH$_3$, and NH$_2$ eliminations, however, there is only one component in the translational energy distribution. A dissociation rate of $(4.5 \pm 1) \times 10^6$ s$^{-1}$ was obtained from the $m/e = 91, 78, 77$, and 76 product growths with respect to the delay time between pump and probe laser pulses. The same dissociation rate suggests the dissociation of these channels must occur in the same electronic state.

Isotope substituted $d$-aniline was also studied. The fragment ion images are shown in Figure 5. It shows that C$_5$D$_4$, corresponding to NH$_2$D elimination is the major products from the ammonia molecular elimination channel. However, small amount of fragments $m/e = 79$ and 78, corresponding to the NHD$_2$ and ND$_3$ elimination were also observed. For amino group elimination, NH$_2$ elimination is the dominant process, as it is shown at $m/e = 82$. But small amount of fragments corresponding to NHD and ND$_2$ elimination were also found. Although fragments of C$_5$D$_3$H, C$_5$D$_2$H$_2$, C$_5$D$_2$H, C$_5$D$_2$, corresponding to the eliminations of NH$_2$D, ND$_2$, NHD, and NH$_2$ have the same masses as those of C$_5$ND$_3$H$_2$, C$_5$ND$_2$H, and C$_5$ND$_2$, corresponding to the eliminations of CD$_3$, CD$_2$H, and CDH$_2$. However, the study of nonisotope labeled aniline suggests that the contribution from methyl group elimination is much smaller than that from ammonia and amino group elimination. In addition, the image intensity distribution of ammonia elimination is very different from that of amino group elimination. They can be separated from each other easily. Similar isotope substituted fragments were also observed in both H atom and H$_2$ elimination channels. In these channels, H atom, HD, and D$_2$ molecule eliminations are the major channels and D atom elimination is the minor channel. However, no H$_2$ elimination was observed. The observation of these fragments indicates the D atom and H atom exchange to some extent prior to dissociation.

The relative intensities of these isotope substituted fragments and their translational energy distributions are shown in Figure 6. Although the translation energy distribution of H atom elimination channel has two components, however, the distribution of D atom elimination channel has only one component, and it decreases monotonically with the increase of energy. It suggests that dissociation mechanisms of H atom and D atom elimination are different. For the analogous H$_2$, NH$_2$, and NH$_3$ elimination channels, the translational energy distributions of these isotope substituted fragments show very similar distributions to each other, indicating the similar dissociation mechanism.

**4-Methylpyridine.** 4-Methylpyridine shows very similar dissociation channels to those of aniline. However, fragment relative intensities are very different. Photofragment ion images from the photodissociation of 4-methylpyridine at 193 nm are shown in Figure 7. The study of photolysis laser power dependence in the region of 7~28 mJ/cm$^2$ showed that $m/e = 90$ and $m/e = 91$ resulted from two photon absorption. Images of $m/e = 92$ and 78 have the largest intensities, they represent two major dissociation channels of 4-methylpyridine, i.e., C$_5$-NH$_4$CH$_3$ → C$_5$NH$_4$CH$_2$ + H, and C$_5$NH$_4$CH$_3$ → C$_5$NH$_4$ + CH$_3$. It is interesting to note that images of $m/e = 77$ and 76 with small intensities were observed. They correspond to the NH$_2$ and NH$_3$ eliminations. In addition, fragment ions with small intensities of $m/e = 66, 54, 53, 52, 41, 40$, and 39 were also observed. However, these signals are very small and they will not be discussed in this work.

The fragment translational energy distributions obtained from the ion image are presented in Figure 8. Compared to the
maximum available energies, the average released translation energies are all very small. They are only 5.4%, 7.1%, 19.4%, and 6.6% of the maximum available energies for H atom, CH\textsubscript{3}, NH\textsubscript{3}, and NH\textsubscript{2} elimination channels, respectively.

The similar dissociation channels were also observed in the photodissociation of d\textsubscript{3}-4-methylpyridine. Photofragment images are shown in Figure 9. m/e = 96 was from parent molecule, m/e = 95 was from the contribution of H atom elimination as well as some incomplete isotope-labeled d\textsubscript{2}-methylpyridine (5%), and m/e = 94 corresponded to the D atom elimination. Photofragments of m/e = 78, 79, 80, and 81 were mainly from C\textsubscript{5}NH\textsubscript{4}, C\textsubscript{5}NH\textsubscript{3}D, C\textsubscript{5}NH\textsubscript{2}D\textsubscript{2}, and C\textsubscript{5}NHD\textsubscript{3}, as a result of CD\textsubscript{3}, CH\textsubscript{2}D, CH\textsubscript{3}D, and CH\textsubscript{4} elimination. Since the ionization potential of NH\textsubscript{2} is larger than the VUV photon energy we used in this work, no amino radicals could be ionized. The relative branching ratios of CHD\textsubscript{2}, CH\textsubscript{2}D, and CH\textsubscript{3} elimination channels can be obtained directly from the intensity of light fragments in order to avoid the interference from ND\textsubscript{2}, NH\textsubscript{D}, and NH\textsubscript{2} eliminations. Fragment ion intensity ratios were found to be CD\textsubscript{3}:CD\textsubscript{2}H:CDH\textsubscript{2}:CH\textsubscript{3} = 91:3:6:4.5:0.9. Since the branching ratios of the analogues NH\textsubscript{3} and NH\textsubscript{2} elimination channels are very small, we did not intend to observe these channels for this isotope-labeled compound. The observation of various D atom substituted methyl radicals indicates that H and D atoms exchange before dissociation.

Dissociation rates of $1.4 \pm 0.8 \times 10^6$ s\textsuperscript{-1} and $1.8 \pm 0.5 \times 10^6$ s\textsuperscript{-1} were obtained from product growths with respect to the delay time between pump and probe laser pulses for C\textsubscript{5}NH\textsubscript{4}CH\textsubscript{3} and C\textsubscript{5}NH\textsubscript{4}CD\textsubscript{3}, respectively. The dissociation rate of C\textsubscript{5}NH\textsubscript{4}CD\textsubscript{3} is only a little slower than that of C\textsubscript{5}NH\textsubscript{4}CH\textsubscript{3}.

IV. Discussion

A. Dissociation and Isomerization Mechanisms. (a) 4-Methylpyridine. Previous studies of methylpyridine mainly focused on the excitation to the S\textsubscript{1} and S\textsubscript{2} states. The fluorescence quantum yield and intersystem crossing quantum yield decrease rapidly with the decrease of photon wavelength from 290 to 250 nm\textsuperscript{26}. Fluorescence quantum yield changes from $10^{-4}$ at 290 nm to less than $2 \times 10^{-6}$ at 250 nm and the quantum yield of intersystem crossing also drops from 0.8 to 0.04. Internal conversion to the ground electronic state becomes the dominant process. However, very little study has been done at the region of 193 nm. Since the methyl group is not an electronic chromophore in this region, UV absorption of 4-methylpyridine at 193 nm only correlates to the excitation of the electrons of the pyridyl ring. The excitation of the pyridyl ring results in an excited state, stable with respect to dissociation. Dissociation must occur either through the coupling of the stable and repulsive states, or after the internal conversion from an initial excited state to a lower electronic state. Since the dissociation in the ground state usually results in a limited release of kinetic energy due to the extensive energy randomization among vibrational degrees of freedom and has a slow dissociation rate, the observation of small kinetic energy release and slow dissociation rate suggest all of the 4-methylpyridine molecules relax to the ground electronic state through internal conversion prior to dissociation.

tion. The results can be represented by the following reactions.

\[
\text{C}_5\text{NH}_4\text{CH}_3 + hv_{193\text{nm}} \rightarrow \text{C}_5\text{NH}_4\text{CH}_3^* \quad \text{(excitation)} \quad (1)
\]

\[
\text{C}_5\text{NH}_4\text{CH}_3^* \rightarrow \text{C}_5\text{NH}_4\text{CH}_3^\dagger \quad \text{(internal conversion to S}_0\text{)} \quad (2)
\]

Here, \(\text{C}_5\text{NH}_4\text{CH}_3^*\) represents 4-methylpyridine in the electronic excited states, and \(\text{C}_5\text{NH}_4\text{CH}_3^\dagger\) represent 4-methylpyridine in the ground electronic state, respectively.

After internal conversion to the ground electronic state, 4-methylpyridine molecules could dissociate through various possible dissociation channels. Statistical transition-state theory has predicted that, given comparable pre-exponential factors for different bond fissions, the reaction pathway with the lowest energetic barrier should dominate the dissociation. Since the C–CH\(_2\) and methyl C–H bond energies are relatively small compared to the other bond energies in the aromatic ring and these dissociation have no exit barrier because of the production of two radicals in the ground electronic state, H atom and CH\(_3\) eliminations are expected to be the major dissociation channels. Indeed, they are the major channels observed in the experiment. These dissociation channels are described by the following reactions.

\[
\text{C}_5\text{NH}_4\text{CH}_3^\dagger \rightarrow \text{C}_5\text{NH}_4\text{CH}_2 + \text{H} \quad \text{(direct dissociation after internal conversion)} \quad (3a)
\]

\[
\text{C}_5\text{NH}_4\text{CH}_3^\dagger \rightarrow \text{C}_5\text{NH}_4 + \text{CH}_3 \quad \text{(direct dissociation after internal conversion)} \quad (3b)
\]

However, the observation of \(\text{C}_6\text{H}_5\) shows that a small fraction of 4-methylpyridine molecules go through a complicated isomerization prior to dissociation. To produce fragment \(\text{C}_6\text{H}_5\) and \(\text{NH}_2\) from 4-methylpyridine, H atoms in the molecule must migrate until nitrogen atom gathers two H atoms and then C–N bond breaks. This involves successive H atom migration and ring isomerization. The similar isomerization must occur in order to generate fragments \(\text{C}_6\text{H}_4\) and \(\text{NH}_3\). Since the minor channels observed in 4-methylpyridine correspond to the major channels in aniline and they have the similar translational energy distributions, some of the 4-methylpyridine must isomerize to aniline before dissociation occurs. A reasonable isomerization mechanism that explains the experimental results is the isomerization similar to that of toluene and xylene found in our previous experiments.22,23 The isomerization starts from the change of 4-methylpyridine to a seven-membered ring isomer.

**Figure 8.** Photofragment translational energy distributions of reactions (a) \(\text{C}_5\text{NH}_4\text{CH}_3 \rightarrow \text{C}_5\text{NH}_4\text{CH}_2 + \text{H}\) (b) \(\text{C}_5\text{NH}_4\text{CH}_3 \rightarrow \text{C}_5\text{NH}_4 + \text{CH}_3\) (c) \(\text{C}_5\text{NH}_4\text{CH}_3 \rightarrow \text{C}_6\text{H}_4 + \text{NH}_3\) (d) \(\text{C}_5\text{NH}_4\text{CH}_3 \rightarrow \text{C}_6\text{H}_5 + \text{NH}_2\). Arrows indicate the maximum available energies in each dissociation channel.

**Figure 9.** Photofragment ion images of d\(_3\)-picoline (a) \(m/e = 15\sim18\) (b) \(m/e = 77\sim96\).
After the isomerization to the seven-membered ring isomer, the exchange of relative nitrogen and carbon atoms’ positions occurs through H migration around the seven-membered ring. In the end, the rearomatization of seven-membered ring to six-membered ring produces both methylypyridine and aniline. The subsequent dissociation produces all kinds of fragments we observed in the experiment.

\[
\text{C}_6\text{H}_4\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2
\]  
(6 to 7 membered ring isomerization) (4)

\[
\text{c-C}_6\text{H}_7\text{NH}_2 \rightarrow \text{c-C}_6\text{H}_7\text{NH}_2
\]  
(H atom migration in 7-membered ring) (5)

\[
\text{c-C}_6\text{H}_7\text{NH}_2 \rightarrow \text{C}_5\text{NH}_4\text{CH}_3
\]  
(rearomatization to methylypyridine) (6a)

\[
\text{c-C}_6\text{H}_7\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2
\]  
(rearomatization to aniline) (6b)

\[
\text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{H}
\]  
(dissociation after rearomatization) (7a)

\[
\text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_5\text{NH}_4 + \text{CH}_3
\]  
(dissociation after rearomatization) (7b)

\[
\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5 + \text{NH}_2
\]  
(dissociation after rearomatization) (7c)

\[
\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5 + \text{NH}_3
\]  
(dissociation after rearomatization) (7d)

\[
\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2
\]  
(dissociation after rearomatization) (7e)

Although reaction 7e was not observed in 4-methylpyridine due to the obstacle of multiphoton dissociation, it is likely to occur since it is one of the major dissociation channels of aniline.

The observation of \(\text{CD}_3\), \(\text{CD}_2\text{H}\), \(\text{CDH}_2\), and \(\text{CH}_3\), from \(\text{d}_1\)-4-methylpyridine indicates some molecules undergo isotope exchange prior to dissociation. These exchanges can be achieved by the H and D atom migration around seven-membered ring in reaction 5. Fragment isotope ratios of \([\text{CH}_3 + \text{CH}_2\text{D} + \text{CHD}_2][\text{CD}_3]\) from \(\text{d}_1\)-4-methylpyridine suggest that 10% of 4-methylpyridine isomerize to seven-membered ring isomers and then rearomatize back to methylypyridine prior to dissociation.

(b) Aniline. Aniline is one of the aromatic molecules that the UV photochemistry has been studied extensively. High-resolution laser induced fluorescence spectroscopy of the \(S_1\) state has been investigated, and the fluorescence lifetime and quantum yield of each vibronic level were obtained.\(^{27}\) It shows that the fluorescence lifetime is about 5–9 ns and quantum yield is 0.1–0.2, depending on the vibronic levels. Intersystem crossing is the main nonradiative process in the \(S_1\) state relaxation. The rate of intersystem crossing as large as \(8.2 \times 10^7 \text{ s}^{-1}\) was found.\(^{27}\) The decay of the triplet state generated from the \(S_1\) state through intersystem crossing is very fast. Triplet state lifetime at the energy level corresponding to band origin of the \(S_1\) state (294 nm) is 5653 ns, but it decreases rapidly as the energy increases. Lifetime as short as 168 ns was observed at energy 3800 cm\(^{-1}\) above the \(S_1\) band origin.\(^{28}\) Although the intersystem crossing rate from \(S_1\) to \(T_1\) is fast, however, no phosphorescence was observed in the gas phase due the rapid decay from \(T_1\) to \(S_0\).

Compared to the studies of the \(S_1\) state, the photochemistry at 193 nm has received little attention. Early experimental investigation\(^{29,30}\) and recent theoretical study\(^{31}\) suggest the absorption of 193 nm photons corresponds to the excitation of electrons of the phenyl ring (\(\pi^* \rightarrow \pi\)). Internal conversion of the phenyl ring electronic excited state at such high energy level usually is very fast. The dissociation therefore is expected to be very similar to that of 4-methylpyridine, i.e., dissociation occurs in the ground state and the channels with low dissociation barrier heights are the dominant processes. Indeed, cleavage through weak chemical bonds such as N−H and C−N bonds were found to be the major dissociation channels. Dissociation occurs in the ground electronic state is further confirmed by the fact that the maximum translational energy release of the \(H_2\) elimination reaches the maximum available energy of the reaction \(\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{H} + \text{H}_2\). Since the fragment with maximum translational energy corresponds to the products \(\text{C}_6\text{H}_5\text{H}_2\) and \(\text{H}_2\) produced in the ground electronic state and the ground state of these two close shell fragments only correlates to the ground state of the parent molecule, the dissociation must result in the ground electronic state.

The observation of fragment \(\text{C}_6\text{H}_4\text{NH}_2\) and \(\text{CH}_3\) from aniline and various isotope-substituted fragments such as \(\text{NH}_2\), \(\text{NH}_2\text{D},\) \(\text{NHD}_2\) from \(\text{d}_5\)-aniline can be explained by the similar isomerization and dissociation mechanism described in 4-methylpyridine, i.e., the isomerization from aniline to seven-membered ring, followed by H and D atom migration in seven-membered ring, and then the rearomatization to both aniline and methylypyridine prior to dissociation.

Although there are many similarities between the dissociation properties of 4-methylpyridine and aniline, however, some difference was also observed. For example, the elimination of close shell molecules, like \(\text{H}_2\), \(\text{NH}_3\), plays a very important role in aniline, but they were not observed in the direct dissociation of 4-methylpyridine. In addition, the fast component in the translational energy distributions of \(H\) atom elimination was only found in aniline. This component must result from the dissociation in the excited state of a repulsive potential, or from an electronic state with a large exit barrier. Since the reverse reaction of \(H\) atom elimination has no barrier in the ground electronic state, the fast component must result from the dissociation in the electronic excited state. Very recently, it was proposed that in several aromatic molecules, a \(\pi^* \rightarrow \pi\) state exists in the vicinity of \(S_1\) state,\(^{32–34}\) and the potential energy surface of this state is essentially a repulsive state along the \(N−\text{H}\) coordinate. It is possible that the fast component of \(H\) atom elimination we observed in the experiment resulted from this state. Since the fragment distribution of the fast component is isotropic, dissociation does not occur directly on the repulsive

potential energy surface. Instead, dissociation must occur indirectly through the coupling between the repulsive surface and other excited states on a time scale much longer than the parent molecule rotation. On the other hand, H atom elimination also has an exit barrier in the triplet state. Dissociation from the triplet state cannot be totally excluded without the additional information about the intersystem crossing quantum yield at this wavelength.

The isomerization and dissociation mechanism of aniline can be summarized as followings.

\[ C_6H_5NH_2 + h\nu_{193nm} \rightarrow C_6H_5NH_2^* \] (excitation) (8)
\[ C_6H_5NH_2^* \rightarrow C_6H_4NH_2^+ (\text{internal conversion to } S_0) \] (9)
\[ C_6H_5NH_2^* \rightarrow C_6H_5NH + H \] (dissociation from excited state) (10)
\[ C_6H_5NH_2^+ \rightarrow C_6H_5NH + H \] (direct dissociation after internal conversion) (11a)
\[ C_6H_5NH_2^+ \rightarrow C_6NH_5 + H_2 \] (direct dissociation after internal conversion) (11b)
\[ C_6H_5NH_2^+ \rightarrow C_6H_5 + NH_2 \] (direct dissociation after internal conversion) (11c)
\[ C_6H_5NH_2^+ \rightarrow C_6H_5 + NH_3 \] (direct dissociation after internal conversion) (11d)
\[ C_5NH_2CH_3^+ \rightarrow C_5C_6NH_7^+ \] (6 to 7 membered ring isomerization) (12)

Reactions following reaction 12 are the same as reactions (5)~(7).

According to this isomerization and dissociation mechanisms, the ratio \([ND_3 + NHD_2]/[NH_2D]\) observed from d5-aniline indicates that 23% of aniline in the ground electronic state isomerize to seven-membered ring, followed by H/D atom migration, and then rearomatize to aniline prior to dissociation.

Although the slow dissociation rates and translational energy distributions obtained from the experimental measurement suggest that both aniline and 4-methylpyridine dissociation occurs on the ground electronic state (except the fast component of H atom elimination in aniline), the possibility that isomerization occurs to some extent in the excited state before molecules reach the ground state through internal conversion cannot be totally excluded. This kind of isomerization, like pyridine undergoes ring opening isomerization in the excited state, has been observed. However, the different intermediates produced directly in the electronic excited state from 4-methylpyridine and aniline, respectively, must be able to isomerize to each other with low enough barrier heights in order to explain the experimental results. Due to the lack of excited-state potential energy surfaces at this moment, there is no compelling evidence to claim their intermediacy in the present case.

**B. Potential Energy Surface.** This particular isomerization between six-membered ring and seven-membered ring is supported by ab initio calculations. The energies of isomers and various transition states along the isomerization and dissociation pathways from ab initio calculation are shown in Figure 10. In the calculation, the geometries were optimization by B3LYP/6-31G* and the energies were calculated by G3 scheme. The dissociation of 4-methylpyridine has barrier heights of 91.0 kcal/mol for C–H bond cleavage, and 105.9 kcal/mol for C–C bond cleavage. The isomerization of 4-methylpyridine to seven-membered ring starts with the H atom shift from methyl group to the carbon atom next to the methyl group, followed by the formation of bicyclo-isomer as an intermediate, and finally the isomerization to form seven-membered ring isomer. The six-membered ring to seven-membered ring isomerization has a barrier height of 88.7 kcal/mol. Since the barrier heights are all very close in energy, isomerization to seven-membered ring competes with C–C bond and C–H bond dissociation. Although most of the 4-methylpyridine molecules dissociate directly through C–C and C–H bond cleavages after the internal conversion, however, experimental data shows that at least 10% of 4-methylpyridine molecules isomerize to seven-membered ring prior to dissociation.

Dissociation and isomerization barrier heights in the ground electronic state of aniline show the similar properties to that of 4-methylpyridine. Eliminations of H atom, H_2, NH_2, NH_3 have barrier heights of 86.4, 104~116, 100.7, and 72 kcal/mol, respectively. Isomerization of aniline to seven-membered ring isomer also starts with the H atom shift from amino group to the carbon atom next to the amino group, forming a bicyclo-intermediate, and then followed by the isomerization to seven-membered ring. The barrier height of the isomerization is only 102.4 kcal/mol, which is very close to various dissociation barrier heights. Isomerization to seven-membered ring therefore competes with the direct dissociation channels in the ground electronic state. Most of the aniline molecules in the ground electronic state dissociate directly, but at least 23% of aniline in the ground-state isomerize to seven-membered ring.

It is interesting to note that there are four different seven-membered ring isomers, depending on the positions of H atoms. Among these isomers, 1-aza-1,3,6-cycloheptatriene and 1-aza-2,4,6-cycloheptatriene can be produced directly from 4-methylpyridine and aniline respectively after the six-membered ring to seven-membered ring isomerization. The other isomers including 1-aza-2,4,7-cycloheptatriene and 1-aza-1,3,5-cyclo-
heptatriene require further H atom migration around the seven-membered ring. For example, 1-aza-1,3,5-cycloheptatriene can be produced from 1-aza-1,3,6-cycloheptatriene through 2,5-H shift, and 4,7-H shift of 1-aza-1,3,5-cycloheptatriene can generate 1-aza-2,4,7-cycloheptatriene. The isomerization between 1-aza-1,3,6-cycloheptatriene and 1-aza-2,4,6-cycloheptatriene can be achieved through 1,5-H shift. The barrier heights between these seven-membered ring isomers are only about 32~40 kcal/mol. Consequently, H and D atoms can easily migrate around the seven-membered ring due to the low barrier heights, resulting in several seven-membered ring isomers. The exchange of H and D atom and the change of relative nitrogen and carbon atoms’ positions all come from these H or D atom migration around the seven-membered ring.

The potential energies corresponding to the elimination of close shell molecules including H2 and NH3 are also shown in Figure 10. NH3 elimination starts from the migration of H atom in the position 2 toward N atom of the amino group, followed by forming the C6H5—NH2 complex, and then NH3 elimination occurs. It has the lowest dissociation threshold. The maximum available energy is as large as 75 kcal/mol. As a result, the photofragment translational energy release in this channel is relatively large.

In contrast to NH3 elimination, there are many dissociation channels leading to H2 elimination. They can be classified into two types of H2 elimination, according to the values of the exit barrier height. The H atoms can be both eliminated from phenyl ring and produce 2-aminobenzene and 3-aminobenzene. The calculation shows that they are endothermic by 80.6 and 83.8 kcal/mol and have the dissociation barriers of 113.4 and 119.3 kcal/mol, respectively. The exit barrier heights for this type of elimination channel are as large as 32.8 and 35.5 kcal/mol, respectively. This type of H2 elimination occurs through the H atom migration in phenyl ring, and then H2 dissociated from the parent molecule through three-center elimination. It is similar to the benzene H2 elimination mechanism.36 Another channel belonging to this type of elimination is the H2 elimination from seven-membered ring. The barrier height is 114.6 kcal/mol, and it is endothermic by 81 kcal/mol. The exit barrier of 33 kcal/mol in this channel is similar to the values in the other two channels. For the other type of H2 elimination, H atoms can be both eliminated from amino group, or one is from amino group and the other is from phenyl ring. This type of H2 elimination has dissociation barriers of 104.2 and 110 kcal/mol and is endothermic by 103.1 and 105.7, respectively. In contrast to the other type of H2 elimination, the exit barriers are small. They are only 1.1 and 4.3 kcal/mol.

The photofragment translational energy distribution of the H2 elimination shows two components, indicating two different dissociation mechanisms. For the fast component, the average released translational energy is large, and the peak of the distribution is located at 23 kcal/mol. It must result from a dissociation channel with large exit barrier, i.e., both H atoms are eliminated from phenyl ring and benzene-like derivatives are produced, or from the seven-membered ring isomer. This can be confirmed from the fact that the maximum translational energy of the fast component reaches the maximum available energies of these reaction C6H5NH2 → C6H3NH2 (or C6H3NH within experimental error) + H2, corresponding to the products C6H3NH2 (or c-C6H5NH3) and H2 produced in the ground electronic state. On the other hand, the slow component has limited translational energy released. It must result from a dissociation channel with small exit barrier, corresponding to both H atoms eliminated from amino group or one from amino group and the other from phenyl ring. However, this type of H2 elimination is less than 10% of the total H2 elimination.

C. Comparison to Photodissociation of Toluene. Toluene has the similar structure to those of methylpyridine and aniline. Since the photophysics and photochemistry processes of toluene have been studied extensively, it is thus interesting to compare the photodissociation of methylpyridine and aniline to that of toluene. Toluene in the S2 state produced by 200 nm excitation was found to undergo fast internal conversion to the S0 and S1 states with a lifetime of ~50 fs.20 Dissociation rate of toluene after 193 nm excitation under collision-free conditions was found to be 2 × 10^6 s−1.22 The fast relaxation from the S2 and S1 states to S0, and the slow dissociation rate suggest the dissociation occurs from the vibrationally excited ground electronic state after internal conversion. In the ground state, 75% of hot toluene dissociate directly through methyl H atom and CH3 elimination. However, 25% of toluene isomerize to seven-membered ring and rearomatize back to toluene, and eventually they all dissociate through H and CH3 elimination channels from six-membered ring. No dissociation from seven-membered ring isomer was observed.

4-methylpyridine has very similar dissociation properties to those of toluene. Most of the 4-methylpyridine dissociates through methyl C—H and C—CH3 bond cleavages after internal conversion. Since seven-membered ring can isomerize to both methylpyridine and aniline, the ratio of [CH+ + CH2D + CHD2]/[CD3] from d4-methylpyridine suggest that more than 10% of 4-methylpyridine molecules isomerize to seven-membered ring and then rearomatize to six-membered ring prior to dissociation. On the other hand, aniline shows different dissociation properties from those of toluene. Excited-state dissociation plays an important role at this photon energy. 75% of H elimination occurs in the electronic excited state. Although the NH2 and H atom eliminations from the ground state and the isomerization to seven-membered ring are analogous to those of toluene, however, the elimination of closed shell molecules, like H2 and NH3 in aniline, were not observed in toluene. Indeed, closed shell molecule elimination channel has not been observed for any alkylbenzenes in this photon energy region.

Compared to 25% of toluene, at least 10% of 4-methylpyridine and more than 23% of aniline in the ground state isomerize to seven-membered ring and then rearomatize to six-membered ring prior to dissociation. The results demonstrate that this isomerization not only plays a very important role in toluene and xylene, but also plays a very important role in nitrogen atom contained aromatic molecules. The significance of this isomerization is that the carbon, nitrogen, and hydrogen atoms belonging to the alkyl or amino group are involved in an exchange with those atoms in the aromatic ring during the isomerization. They cannot be achieved by the other isomerization.

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