H and CH₃ eliminations in the photodissociation of chlorotoluene

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Photodissociation of o-, m-, and p-chlorotoluene at 193 nm under collision-free conditions has been studied using multimass ion imaging techniques. In addition to the Cl atom elimination, photofragments corresponding to the reactions of C₆H₄ClCH₃ → C₆H₄ClCH₂⁺ + H and C₆H₄ClCH₃ → C₆H₄Cl + CH₃ were observed. Dissociation rates and fragment translational energy distributions were measured. A comparison with RRKM calculation has been made and the possible dissociation mechanism was discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1609393]

I. INTRODUCTION

Photodissociation of phenyl halides (–Cl, –Br, –I) have been studied extensively. They show very simple dissociation dynamics compared to the other aromatic molecules. Ultraviolet (UV) absorption of the phenyl halides (–Cl, –Br, –I) in the 190 nm ~ 250 nm region corresponds to the excitations of electrons of the phenyl ring and the nonbonding electron of the halogen atoms. The nonbonding electron excitation of the halogen atoms leads to direct dissociation, that is, an immediate release of halogen atoms on a repulsive surface. Alternately, the excitation of the phenyl ring results in an excited state, stable with respect to dissociation. Dissociation occurs indirectly either through the coupling of the stable and repulsive state, or after the internal conversion from an initial excited state to a lower electronic state. Direct dissociation is fast and releases a large amount of kinetic energy. Indirect dissociation 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. 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 indirect dissociation. Since the C–X (X = Cl, Br, I) bond energy is relatively small, halogen atom elimination is expected to be the major channel in the indirect dissociation. In the photodissociation of iodobenzene,1,2 bromobenzene,2,3 chlorobenzene,2,4–7 o-, m-, p-chlorotoluene,9–11 and o-, m-, and p-dichlorobenzene,9,12,13 halogen atom elimination was indeed found to be the only dissociation channel in these molecules, and both direct and indirect dissociation have been observed. As a result, some of these molecules are frequently used as precursors to generate phenyl and benzyl radicals.

In this work, we report the photodissociation of o-, m-, and p-chlorotoluene at 193 nm in a molecular beam using multimass ion imaging techniques. In addition to the Cl atom elimination, H atom and CH₃ elimination were also observed. The possible dissociation mechanism was discussed.

II. EXPERIMENT

The experimental techniques have been described in detail in our previous reports on other aromatic molecules,14–16 and only a brief description is given here. Chlorotoluene vapor was formed by flowing ultrapure Ar at pressures of 300 Torr through a reservoir filled with liquid sample at 20 °C. The chlorotoluene/Ar mixture was then expanded through a 500 μm high temperature (80 °C) pulsed nozzle to form the molecular beam. Molecules in the molecular beam were photodissociated by a 193 nm UV laser pulse, and then ionized by a 118 nm VUV laser pulse. The distance and time delay between the vacuum-ultraviolet (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 photoinitiation. 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. 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 setup is shown in Fig. 1. The dissociation rate was obtained from the product growth with respect to the delay time between the pump and probe laser pulses using time-of-flight mass spectrometer.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the photofragment ion image of m/e = 91, resulting from Cl atom elimination of p-chlorotoluene. The translation energy distribution, as illustrated in Fig. 2(b), clearly demonstrates that it contains three components. These three components have been observed in previous study.9 The fast component was assigned to be the direct dissociation from a repulsive state. The medium component was due to the dissociation from the triplet state, and the slow component resulted from the dissociation via highly vibrational levels of the ground electronic state.

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In addition to the fragment $\text{C}_6\text{H}_4\text{CH}_3$, fragments of $\text{C}_6\text{H}_4\text{ClCH}_2$, $\text{C}_6\text{H}_4\text{Cl}$, and $\text{CH}_3$ were also observed from the photodissociation of $p$-chlorotoluene. They suggest the existence of the other dissociation channels. Figure 3(a) shows the images of $m/e = 125–129$. Images of $m/e = 126$ and 128 are the parent molecules $\text{C}_6\text{H}_4\text{ClCH}_3$ of isotope $^{35}\text{Cl}$ and $^{37}\text{Cl}$, respectively. $m/e = 129$ is the $^{12}\text{C}$ isotope of parent molecule. Images of $m/e = 125$ and 127 are photofragments $\text{C}_6\text{H}_4^{35}\text{ClCH}_2$ and $\text{C}_6\text{H}_4^{37}\text{ClCH}_2$, resulting from H atom elimination. The translation energy distribution, as illustrated in Fig. 3(b), shows that the average translational energy released is small and the maximum translational energy is much less than the available energy. Figures 4(a) and 4(b) show the image of $m/e = 111, 113,$ and 15, corresponding to the photofragments of $\text{C}_6\text{H}_4^{35}\text{Cl}$, $\text{C}_6\text{H}_4^{37}\text{Cl}$, and $\text{CH}_3$. The momentum match of these two fragments further confirms that this fragment pair is from the dissociation of $p$-$\text{C}_6\text{H}_4\text{ClCH}_3$. The translational energy distribution, as illustrated in Fig. 4(c), shows the similar properties to those of the H atom elimination channel. These are the typical characteristics of the indirect dissociation from a molecule undergo internal conversion to a lower electronic state with no exit barrier.

A 193 nm photolysis laser fluence dependence measurement was carried out in the region from 0.14 mJ/cm$^2$ to 5.9 mJ/cm$^2$. The shapes of these images described above do not change with photolysis laser intensity and the image intensities are proportional to the laser fluence. These measurements suggest that they all resulted from one-photon absorption.

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 the paper; (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 Y axis is mass axis, and X axis (perpendicular to the plane of the paper) is the velocity axis.

FIG. 2. (a) Image of $m/e = 91$. (b) Photofragment translational energy distribution of reaction $p$-$\text{C}_6\text{H}_4\text{ClCH}_3 \rightarrow \text{C}_6\text{H}_4\text{CH}_3 + \text{Cl}$.

FIG. 3. (a) Images of $m/e = 125–129$. (b) Photofragment translational energy distribution of reaction $p$-$\text{C}_6\text{H}_4\text{ClCH}_3 \rightarrow \text{C}_6\text{H}_4\text{ClCH}_2 + \text{H}$.

FIG. 4. (a) Images of $m/e = 111, 113$. (b) Image of $m/e = 15$. (c) Photofragment translational energy distribution of reaction $p$-$\text{C}_6\text{H}_4\text{ClCH}_3 \rightarrow \text{C}_6\text{H}_4\text{Cl} + \text{CH}_3$. 

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The fragment ion intensity ratios between C₆H₄ClCH₂, C₆H₄CH₃ (slow), C₆H₄CH₃ (medium), C₆H₄CH₃ (fast), C₆H₄Cl, and CH₃ from the photodissociation of p-chlorotoluene are listed in Table I. These values have been corrected for the fragment velocity effect. The branching ratios can be obtained directly from the normalization of these values by the ionization cross sections at this wavelength. This ratio can be used to calculate the relative cross sections of these two fragments at this VUV laser intensity gives a good estimation of the relative ionization potential of these two fragments, the relative ionization potential of these two fragments. The relative branching ratio of the Cl elimination and CH₃ elimination can be estimated by the following argument. In the photodissociation of xylene, one of the major channels is C₆H₄CH₂CH₃ → C₆H₄CH₃ + CH₃. ¹⁷ The relative ion intensity of C₆H₄CH₃⁺ and CH₃⁺ measured by the same VUV wavelength (118.2 nm) is 10:2 ± 1. Since these two fragments are resulted from the same dissociation channel of xylene and the VUV photon energy is much higher than the ionization potential of these two fragments, the relative ion intensity gives a good estimation of the relative ionization cross sections of these two fragments at this VUV laser wavelength. This ratio can be used to calculate the relative branching ratio between the C₆H₄CH₂CH₃ → C₆H₄Cl + CH₃ channel and the C₆H₄CH₂CH₃ → C₆H₄CH₃ + Cl channel. The ratio of C₆H₄CH₂CH₃⁺ and CH₃⁺ that we measured in the photodissociation of p-chlorotoluene is 106±20. This ratio after normalization by the ionization cross sections obtained from xylene is 23±15. In the other word, the CH₃ elimination channel is about 2–12% of the Cl atom elimination channel. Although we do not have the ionization cross sections to estimate the branching ratio for H atom elimination channel, the relatively large ion intensity ratio between C₆H₄CH₂ and C₆H₄CH₃ suggests H atom elimination must also play an important role in the photodissociation of p-chlorotoluene.

The dissociation rate of p-chlorotoluene produced from 193 nm excitation was measured from the product growth as a function of delay time between pump and probe laser pulses. A value of (1.2±0.2)×10⁶ s⁻¹ was obtained, as shown in Fig. 5. The same value obtained from fragments m/e = 15, 111, and 125 indicates that they all resulted from the same electronic state. The small translational energy released and slow dissociation rate suggest that the dissociation occurs most likely in the ground electronic state. Similar results were also observed in the photodissociation of m, o-chlorotoluene. The experimental measurements are summarized in Table I.

The dissociation of chlorotoluene in the ground electronic state is standard unimolecular reactions. They can be characterized by RRKM calculation. We used the potential energy surface obtained from ab initio calculation and performed the variational RRKM calculation for various reactions of p-chlorotoluene. All ab initio calculations were done with the GAUSSIAN 98 program. The geometry optimization and vibrational frequencies of the reactants, transition states, and products were calculated by using B3LYP/6-311 + G(d,p) level. The bond energies from calculation are 90.7 kcal/mol, 86.4 kcal/mol, and 99.0 kcal/mol for C₆H₄H–Cl, C₆H₄ClCH₂–H, and C₆H₄Cl–CH₃, respectively. The results of RRKM calculation show that the dissociation rates for Cl, H, and CH₃ eliminations in the ground state are 1×10⁴ s⁻¹, 7×10⁴ s⁻¹, and 5×10⁵ s⁻¹, respectively. The total dissociation rate from calculation was found to be close to the experimental values, although it overestimates the CH₃ elimination channel.

Compared to most of the previous studies which focused on the dissociation mechanism of Cl atom elimination and for which only Cl atom elimination channel was reported,

FIG. 5. Product buildup times from photodissociation of p-C₆H₄ClCH₃. (a) C₆H₄ClCH₂, (b) C₆H₄Cl, (c) CH₃.

<table>
<thead>
<tr>
<th>p-chlorotoluene</th>
<th>m-chlorotoluene</th>
<th>o-chlorotoluene</th>
<th>RRKM</th>
</tr>
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<tbody>
<tr>
<td>C₆H₄ClCH₂</td>
<td>0.36</td>
<td>0.226</td>
<td>0.07</td>
</tr>
<tr>
<td>C₆H₄CH₃(slow)</td>
<td>0.44</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>C₆H₄CH₃(medium)</td>
<td>1</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>C₆H₄CH₃(fast)</td>
<td>0.37</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>C₆H₄Cl</td>
<td>0.06</td>
<td>0.034</td>
<td>0.5</td>
</tr>
<tr>
<td>CH₃</td>
<td>0.017</td>
<td>0.015</td>
<td>0.5</td>
</tr>
<tr>
<td>Rate (s⁻¹)</td>
<td>1.2×10⁶</td>
<td>1.1×10⁶</td>
<td>1.5×10⁶</td>
</tr>
</tbody>
</table>

¹²Dissociate rates in the ground state.
¹³Ion intensity ratios from experimental measurement.
¹⁴p-chlorotoluene branching ratios from RRKM calculation.
our experiments demonstrated the existence of the other dissociation channels. Although H and CH$_3$ eliminations are not the major channels, they cannot be neglected. The similar dissociation channels in $p$, $m$, and $o$-chlorotoluene are due to the similar C–Cl bond strength. However, since the C–I and C–Br bond energies are much smaller than that of C–Cl bond, halogen atom eliminations are expected to be more competitive in iodotoluene and bromotoluene than that in chlorotoluene. Therefore, the H and CH$_3$ eliminations must be less important in these molecules.

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