Unimolecular and Photoinduced Dissociations of Aromatic C₈H₁₀⁺ Molecular Ions

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Production of C₇H₇⁺ in the unimolecular and photoinduced dissociations of ethylbenzene; methylcycloheptatriene; and o-, m-, and p-xylene ions has been investigated using mass-analyzed ion kinetic energy spectrometry. Both the benzylium and tropylium ions were produced near the reaction threshold, whereas only the benzylium ion was observed at higher internal energy achieved by photoabsorption. Experimental data suggest that interconversion between ethylbenzene and methylcycloheptatriene ions occurs more rapidly than their dissociations near the reaction threshold, whereas xylene ions undergo rate-determining isomerization to the methylcycloheptatriene structure, and dissociation occurs from the ethylbenzene/methylcycloheptatriene ion mixture. The processes occurring at higher internal energy are quite similar, except that the tropylium channel cannot compete against the benzylium channel because either the ethylbenzene ion-to-methylcycloheptatriene ion conversion or the dissociation of the methylcycloheptatriene ion to the tropylium ion is slower than the direct dissociation of the ethylbenzene ion. The above mechanistic picture is in disagreement with the prediction of a dynamic model reported previously. A series of investigations performed for the production of C₇H₇⁺ from alkylbenzene ions shows an interesting trend of increasing benzylium production with the increase in the total number of carbon atoms in the alkyl substituents.

1. Introduction

Production of C₇H₇⁺ from various molecular ions, alkylbenzene ions in particular, has been the subject of numerous experimental and theoretical studies in the field of gas-phase ion chemistry. The main focus of these studies has been the isomeric compositions of the C₇H₇⁺ ions generated and the associated mechanistic pathways. Among the several possible isomeric forms of C₇H₇⁺, the benzylium (Bz⁺, 1) and tropylium (Tr⁺, 2) ions have been found to be the most important products in the dissociation of alkylbenzene ions near the threshold energy.

In the case of the toluene ion, both of these are known to be produced: Bz⁺ via simple bond cleavage and Tr⁺ via isomerization to and simple bond cleavage from the cycloheptatriene ion. It is also known that interconversion between toluene and cycloheptatriene ions is rapid near the threshold for hydrogen loss. On the other hand, Bz⁺ was found to be produced preferentially from n-propyl- and n-butylbenzene ions. A molecular orbital calculation and an estimate of the rate-energy relations for the dissociation of the n-propylbenzene ion showed that isomerization to the cycloheptatriene ion could not compete effectively with the direct cleavage to Bz⁺. This was because the isomerization barrier height, which was lower than that for direct cleavage in the toluene ion case, is comparable to the latter in the n-propylbenzene ion case. A similar argument is expected to hold for the dissociation of alkylbenzene ions with larger alkyl chains.

Not mentioned so far is the dissociation of the aromatic C₈H₁₀⁺ ions, namely, ethylbenzene (EB⁺⁺); 7-methylcycloheptatriene (MC⁺⁺); and o-, m-, and p-xylene (pXL⁺⁺, etc.) ions, which have been widely investigated also. Williams and co-workers observed that the average kinetic energy releases in the metastable ion decompositions (MIDs) of EB⁺⁺ and MC⁺⁺ were essentially the same and postulated that isomerization between these structures must be rapid and that both EB⁺⁺ and MC⁺⁺ dissociate to Tr⁺. Groteneyer and Grützmacher carried out an extensive mass spectrometric study of these ions using C- and D-labeled compounds. Also performed were semi-empirical molecular orbital calculations for structures along various reaction paths. It was found that Tr⁺ + CH₃⁺ was lower (by ~0.5 eV) in energy than Bz⁺ + CH₃⁺ and, hence, assumed to be the dominant dissociation channel, in agreement with Williams and co-workers. On the other hand, analysis of the product ion structure utilizing chemical reactivity of Bz⁺ with toluene in an ion cyclotron resonance spectrometer by Ausloos and collision-induced dissociation study by Holmes and co-workers suggested that both Tr⁺ and Bz⁺ were produced near the threshold. Considering the trend described above that both Bz⁺ and Tr⁺ are produced from the tolueene ion while n-propyl- and n-butylbenzene ions produce Bz⁺ only, it is likely that EB⁺⁺ and MC⁺⁺ produce Bz⁺ in addition to Tr⁺.

In this work, the kinetic energy release distributions (KERDs) for the unimolecular dissociations of EB⁺⁺; MC⁺⁺; and o-, m-,
and \( p \)-xylene ions near the threshold, or MID, were analyzed in detail to find evidence for the production of \( Bz^+ \) and \( Tr^+ \). This approach is advantageous in the sense that KERD depends on the dissociation step only and is not affected by isomerization processes which may occur before or after the dissociation. Photodissociation (PD) kinetics experiments were also performed to gain further information on the isomerization processes.

2. Experimental Section

A double focusing mass spectrometer with reversed geometry (VG Analytical model ZAB-E) modified for PD study was used. \(^{15} \) Samples were introduced into the ion source via a septum inlet and ionized by 70 eV electron ionization or by charge exchange ionization using \( CS_2 \) as the reagent gas. Molecular ions generated in the ion source at 180 °C in electron ionization or at 140 °C in charge exchange ionization were accelerated to 8 keV and mass-separated by the magnetic sector. Then, the translational kinetic energy of a product ion generated in the electric sector. This is called the mass-analyzed ion kinetic energy spectrometry (MIKES). Two different modes of dissociation of the molecular ions, MID and PD, were investigated. To generate the molecular ions for the MID study, 70 eV electron ionization was used. For the PD study, the charge exchange ionization was used.

The PD technique developed in this laboratory for the study of ion dissociation dynamics was described in detail previously. \(^{15} \) Briefly, the molecular ion beam was crossed perpendicularly by a laser beam inside an electrode assembly located near the intermediate focal point of the instrument. The 514.5 and 488.0 nm lines of an argon ion laser (Spectra Physics model 164-09) were used for PD of the molecular ions. A MIKE spectrum for PD, or a PD-MIKE spectrum, is often contaminated by contributions from the same reactions occurring unimolecularly (MID) or by collision of the precursor ions with the residual gas. Hence, phase-sensitive detection was adopted to record a MIKE spectrum originating only from PD. To improve the quality of MIKE spectra, signal averaging was carried out for repetitive scans. Errors quoted in this work were estimated from several duplicate experiments at the 95% confidence limit.

7-Methylcycloheptatriene was synthesized according to the methods of Harrison et al. \(^{16} \) and Conrow \(^{17} \) and purified by distillation. Its structure was identified using the \(^1H \) NMR and normal mass spectra. \(^{19} \) Other compounds were purchased from Aldrich and used without further purification.

3. Results and Discussion

For dissociation, both MID and PD, of all of the \( C_8H_{10} \) isomers investigated in this work, methyl loss was the dominant channel (>95% of the total). Scheme 1 shows possible pathways for isomerization and dissociation of \( C_8H_{10} \) isomers (to be confirmed experimentally in this work). Dissociation of a xylene ion to a tolyl ion is not thought to be important near the reaction threshold (to be explained). The pathways for the ortho and meta isomers of the xylene ion are likely to be similar to the para case, as will be confirmed later. Throughout the work, the results for the para isomer will be discussed almost exclusively.

**Energetics.** Thermochemical data \(^{20} - 24 \) for the important neutral and ionic species relevant to the present study are listed in Table 1. Because the thermochemical data for \( MC^{**} \) is not available in the literature, its energy relative to \( EB^{**} \) was estimated by comparing energies of these ions obtained by electronic structure calculations at the HF/6-31G** level and also at the B3LYP/6-31G** level of the density-functional theory. \(^{25} \) These are 77.2 and 60.8 kJ mol\(^{-1} \) at the HF/6-31G** and B3LYP/6-31G** levels, respectively, which are larger than 42 kJ mol\(^{-1} \) at the MNDO level reported by Grotzemeier and Grützmacher. \(^{13} \) The energy of the products \( Tr^+ + CH_3^+ \) was calculated at the same levels. The transition state for the reaction \( MC^{**} \rightarrow Tr^+ + CH_3^+ \) was also found. The height of the reverse barrier was 40 and 1 kJ mol\(^{-1} \) respectively at the HF/6-31G** and B3LYP/6-31G** levels. In our previous study on the toluene ion, \(^{8} \) the reverse barrier in the dissociation of the cycloheptatriene ion to \( Tr^+ + H^+ \) calculated at the HF level, 27.0 kJ mol\(^{-1} \), was in excellent agreement with the G2 result of 26.1 kJ mol\(^{-1} \), whereas the B3LYP/6-31G** calculation \(^{26} \) resulted in a smaller barrier (11.1 kJ mol\(^{-1} \)). More importantly, a classical trajectory calculation on the HF potential-energy surface resulted in KERD that was in good qualitative agreement with the experimental one. \(^{8} \) Assuming that the same trend holds for the present system, the HF/6-31G** result will be adopted here for the transition state connecting \( C_8H_{10}^{**} \) isomers could not be located beyond the semiempirical levels, and their energies drawn as dashed line in the figure have no quantitative meaning.

**Kinetic Energy Release Distribution (KERD).** Unimolecular Dissociation. Figure 2a shows the MIKE spectral profiles for the unimolecular dissociation (\( CH_3^+ \) loss) of \( EB^{**} \) and \( pXL^{**} \)
recorded with the electrode assembly floated at 2.0 kV. The corresponding MIKE profile for MC$^+$ was essentially identical to that of EB$^+$ and those for the o- and m-xylene ions to that of pXL$^+$ and are not shown. As can be seen in the figure, the spectral profiles for EB$^+$ and pXL$^+$ are very similar also, with the pXL$^+$ profile being slightly broader. The method developed in this laboratory$^{27}$ to evaluate KERDs from a MIKE profile introduces some fluctuation originating from high-frequency noise in the spectrum and may not be adequate to see the tiny difference in KERDs of the two reactions. In this work, we recorded the MIKE profiles with the parent ion resolution of $2.8 \text{ eV}$ such that deconvolution of the instrumental broadening was not needed. Because the kinetic energy releases were quite small, such that the instrumental discrimination effect was not important,$^{28}$ the method developed by Holmes and Osborne$^{29}$ was used to evaluate KERDs by fitting the MIKE profiles to the symmetric function

$$y = e^{-ax^2}(1 + b_2x^2 + b_4x^4 + b_6x^6)$$  \hspace{1cm} (4)$$

Here, $y$ is the MIKE profile normalized at the peak height and $x$ is the translational energy referred to the center of the profile. The KERDs thus obtained from the MIKE profiles in Figure 2a are shown in Figure 3 parts a and b. It is to be noted that KERDs in these figures display very similar pattern. In fact, the main purpose of using the noise-free approach in the profile analysis was more to demonstrate the striking similarity in KERDs obtained from all of the five precursor ions than to see the minor difference between KERDs.

Also noticeable in Figure 3 parts a and b is that these KERDs are clearly bimodal, namely, that two different dissociation processes are involved. The production of tolyl ions is much more endothermic than the production of Bz$^+$ and Tr$^+$ and can be neglected for dissociation near the threshold (see Figure 1). Then, it is likely that the latter two channels, namely, reactions 1 and 2, are involved in the dissociation step. Because the production of Tr$^+$ is associated with some reverse barrier, whereas that of Bz$^+$ is a simple bond cleavage occurring without a reverse barrier, it is reasonable to relate the former to the features appearing at higher energy parts of KERDs and the latter to those at lower energy. The same assignments were made previously for bimodal KERDs observed in the dissociation of other aromatic ions.$^{8, 30}$

An experimental KERD appearing bimodal can be separated into two components using the surprisal analysis.$^{31}$ The surprisal factor $I$, a measure of the extent of deviation of a distribution from a prior expectation, is defined as follows:

$$I(T) = -\ln[n(T)/n_0(T)]$$  \hspace{1cm} (5)
Figure 3. KERDs of C$_2$H$_4^+$ generated by unimolecular dissociation (MID) of (a) EB$^{+*}$ and (b) pXL$^{+*}$ are shown as solid curves. Bz$^+$ and Tr$^+$ components in MID-KERDs separated by the surprisal analysis are shown as open (O) and solid (●) circles, respectively. KERD in PD of EB$^{+*}$ at 514.5 nm is shown in (c) as a solid line together with the KERD calculated with the phase space theory (open circles).

Here, $n(T)$ and $n_0(T)$ represent the experimental and expected KERDs, respectively. It is usual to use a KERD calculated by statistical theories as $n_0(T)$. Because the kinetic energy release distribution in the production of Bz$^+$, which is a simple bond cleavage occurring without reverse barrier, is expected to be well described by statistical theories, we calculated this with the phase space theory (PST)\textsuperscript{32} as follows and used it as $n_0(T)$:

$$n(T,J,E) \propto \int_{R_m}^{E-E_0-T} \rho(E - E_0 - R)P(T,J,R)\,dR \quad (6)$$

Here, $n(T,J,E)$ is the KERD at the angular momentum $J$ and the internal energy $E$. The root-mean-square average $J$ evaluated at the ion source temperature was used. $\rho$ and $P$ are product vibrational and angular momentum state densities, respectively. $R$ is the product rotational energy and $R_m$ is its minimum. $E_0$, the reaction critical energy, was set equal to the reaction endoergicity at 0 K, assuming a completely loose transition state. Its best estimate from the thermochemical data listed in Table 1 was 1.74 eV. Other molecular parameters used for the calculation are listed in Table 2. The internal energy of EB$^{+*}$ undergoing MID can be estimated reliably when an accurate rate-energy relation is known.\textsuperscript{33} Because this is not available, a rough estimation was made based on the rate constant data obtained by PD of EB$^{+*}$ (see below) in this work. It was about 2.4 eV. The surprisal plot for the methyl loss of EB$^{+*}$ was found to be 2.4 eV. The surprisal plot for the methyl loss of EB$^{+*}$ is shown in Figure 4.

**Figure 4.** Surprisal plot for the experimental MID-KERD in Figure 3a. The slopes of the lines A and B are 3.1 ± 1.0 and −8.1 ± 0.9, respectively.

**TABLE 2: Molecular Parameters Used in the Calculations of KERDs and Thermal Energy Distributions\textsuperscript{*}**

<table>
<thead>
<tr>
<th>Vibrational Frequencies (cm$^{-1}$)</th>
<th>Polarizability (10$^{-24}$ cm$^3$)</th>
</tr>
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<tbody>
<tr>
<td>pXL$^{+*}$</td>
<td>56, 57, 104, 241, 275, 345, 355, 392, 461, 511, 618, 653, 759, 793, 812, 894, 965, 973, 979, 1002, 1009, 1013, 1098, 1117, 1158, 1180, 1256, 1260, 1364, 1369, 1370, 1401, 1421, 1421, 1428, 1435, 1464, 1586, 1856, 2844, 2844, 2899, 2899, 2959, 2959, 3011, 3013, 3030, 3031</td>
</tr>
<tr>
<td>EB$^{+*}$</td>
<td>41, 103, 198, 239, 339, 349, 394, 420, 488, 620, 715, 769, 770, 791, 890, 912, 918, 949, 996, 998, 1003, 1049, 1105, 1156, 1162, 1200, 1276, 1277, 1312, 1350, 1379, 1407, 1443, 1446, 1466, 1479, 1591, 2863, 2880, 2924, 2941, 2947, 3016, 3020, 3024, 3032, 3036</td>
</tr>
<tr>
<td>Bz$^+$</td>
<td>163, 337, 342, 407, 510, 582, 611, 628, 778, 782, 843, 946, 963, 976, 1000, 1012, 1046, 1089, 1112, 1134, 1157, 1307, 1311, 1326, 1420, 1452, 1540, 1547, 1583, 2975, 3011, 3015, 3017, 3036, 3039, 3067</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>304, 1365, 1365, 2911, 3072, 3072</td>
</tr>
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</table>

*HF/6-31G** results. All frequencies are scaled by 0.89.\textsuperscript{33}
is certainly larger than 1 kJ mol\(^{-1}\) obtained in the B3LYP/6-31G** calculation. Of course, this does not mean that the experimental results are compatible with the reverse barrier (40 kJ mol\(^{-1}\)) obtained in the HF/6-31G** calculation. In the case of the dissociation of CsH\(_{10}\)+\(^{¥}\) generated from ethylbenzene and methylcycloheptatriene, the small KER component was 66% of the total. More importantly, the fact that KERDs for these reactions are identical within the experimental error limit indicates that the isomerization between EB\(^{¥}\) and MC\(^{¥}\) occurs rapidly at the internal energy needed for the observation of MID. This is in agreement with the postulation by Williams and co-workers,\(^{12}\) even though the fact that the Bz\(^{+}\) channel is present in conflict with the Tr\(^{+}\)-only postulation suggested by these investigators.

A surprisal analysis for the dissociation of pXL\(^{+}\) gives nearly the same results as for EB\(^{+}\). The fractions of the small and large KER components and the average kinetic energy releases for each component for dissociations of EB\(^{+}\) and pXL\(^{+}\) are compared in Table 3. Each value in the table will depend on the experimental condition and may not be accurate enough. However, these were obtained through the same treatment of experimental data obtained at the identical condition and have good precision in a relative sense. Hence, it seems to be safe to say that the Bz\(^{+}\)/Tr\(^{+}\) ratios are essentially the same for dissociations of EB\(^{+}\) and pXL\(^{+}\) and that pXL\(^{+}\) dissociates via the same channels as EB\(^{+}\) but at an internal energy a few to several tenths of an electronvolt higher than that of EB\(^{+}\). This is in agreement with the postulation by Williams and co-workers,\(^{12}\) even though the fact that the Bz\(^{+}\) channel is present was mentioned earlier (mechanism 1) or the “H ring-walk” mechanism (mechanism 3) is energetically possible in PD of C\(_{8}\)H\(_{10}\)\(^+\). Its PD rate constant was estimated roughly with the Rice–Ramsperger–Kassel–Marcus (RRKM) theory,\(^{34}\) which was less than 10\(^{-2}\) s\(^{-1}\). Such a slow process cannot be detected at all with the present apparatus. In fact, the PD rate constant of pXL\(^{+}\) determined experimentally (see below) was larger than the above by several orders of magnitude. This rules out the possibility of the tolyl ion production.

We recorded the PD-MIKE spectrum of pXL\(^{+}\), and other xylene isomeric ions also, at 488.0 nm (not shown) and calculated the KERD. These were essentially the same as the PD-KERD for EB\(^{+}\) at 514.5 nm (Figure 3c) within the error limit. According to Figure 1, production of tolyl ions (reaction 3) is energetically possible in PD of C\(_{8}\)H\(_{10}\)\(^+\). Its PD rate constant was estimated roughly with the Rice–Ramsperger–Kassel–Marcus (RRKM) theory,\(^{34}\) which was less than 10\(^{-2}\) s\(^{-1}\). Such a slow process cannot be detected at all with the present apparatus. In fact, the PD rate constant of pXL\(^{+}\) determined experimentally (see below) was larger than the above by several orders of magnitude. This rules out the possibility of the tolyl ion production.

As shown in Figure 1, the energy available in PD of pXL\(^{+}\) in the production of Bz\(^{+}\) + CH\(_{3}\) at 488.0 nm, 2.27 eV, is almost the same as that of EB\(^{+}\) at 514.5 nm, 2.28 eV. Then, essentially identical KERDs in PD of EB\(^{+}\) and pXL\(^{+}\) are nearly the same internal energy suggest that PD of pXL\(^{+}\) also generates Bz\(^{+}\) + CH\(_{3}\), possibly via the same mechanism as in MID. Groteleyer and Grützmacher calculated the potential-energy diagram for the “H ring-walk” mechanism of pXL\(^{+}\) using the MNDO method (Scheme 2).\(^{13}\)

They also calculated the overall rate-energy relation for the production of Bz\(^{+}\) + CH\(_{3}\) via this mechanism and suggested that this pathway be dominant at the internal energy higher than the metastable window. It is difficult to judge which of the two mechanisms, pXL\(^{+}\) \(\rightarrow\) MC\(^{+}\) \(\rightarrow\) EB\(^{+}\) \(\rightarrow\) Bz\(^{+}\) + CH\(_{3}\) (mechanism 1) or the “H ring-walk” mechanism (mechanism 2), are responsible for the methyl loss of pXL\(^{+}\) in PD. In both mechanisms, the final steps, which determine the kinetic energy release, are simple bond cleavages to Bz\(^{+}\) + CH\(_{3}\). If both of these proceed statistically, as was confirmed for mechanism 1 (Figure 3c), one would expect similar KERD regardless of the mechanism. Even though the rate-energy data calculated at the MNDO level favors mechanism 2, we do not have much faith in the reliability of the rate-energy data calculated with the MNDO results. This is because they are not compatible with

\[
E = RE - IE + E_{th} + h\nu
\]

Here, RE and IE are the recombination energy of CS\(_{2}\)\(^{+}\) and the ionization energy of ethylbenzene, the best literature values of which are 10.07\(^{35}\) and 8.77\(^{32}\) eV (971.6 and 846 kJ mol\(^{-1}\)), respectively. E\(_{th}\) is the thermal internal energy at the ion source temperature of 140 °C. Its average, 0.31 eV, was calculated using the molecular parameters in Table 2.\(^{15}\) The average internal energy of EB\(^{+}\) photoexcited at 514.5 nm estimated with eq 7 is 4.02 eV. The PST-KERD for PD at 514.5 nm is shown in Figure 3c, which agrees well with the experimental KERD, indicating that the Bz\(^{+}\) channel is the main pathway, as assumed. Namely, the Bz\(^{+}\) channel is the dominant pathway at ~2.3 eV above the threshold (PD), even though the Tr\(^{+}\) channel can compete effectively at several tenths of an eV above the threshold (MID). We could not perform a PD experiment for MC\(^+\) with well-defined internal energy. For example, most of MC\(^+\) generated by charge exchange with CS\(_{2}\)\(^{+}\) fragmented in the ion source.

TABLE 3: Small and Large Kinetic Energy Release (KER) Components in the Unimolecular Dissociation (MID) of Ethylbenzene (EB\(^{+}\)) and p-Xylene (pXL\(^{+}\)) Ions Separated by Surprisal Analysis

<table>
<thead>
<tr>
<th></th>
<th>EB(^{+})</th>
<th>pXL(^{+})</th>
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<tbody>
<tr>
<td></td>
<td>small KER</td>
<td>large KER</td>
</tr>
<tr>
<td>fraction (%)</td>
<td>66</td>
<td>34</td>
</tr>
<tr>
<td>average KER (eV)</td>
<td>0.050</td>
<td>0.203</td>
</tr>
</tbody>
</table>

KERS evaluated from this profile is in Figure 3c. Unlike its MID counterpart (Figure 3a), the KERD in PD looks monotonic and indicates that the Tr\(^{+}\) channel does not contribute significantly in this case. To see if the Bz\(^{+}\) channel is the main pathway, the KERD was calculated for this channel using phase space theory. Because the molecular ion for PD was generated by charge exchange with CS\(_{2}\)\(^{+}\), its internal energy after photoexcitation can be estimated as follows:

\[
E = RE - IE + E_{th} + h\nu
\]
the present experimental results as mentioned above. Even though we attempted to reproduce the reaction pathways at higher levels and to obtain more reliable rate-energy data, we could not locate most of the transition states. However, we could locate the transition state for the final step of the dissociation via the “H ring-walk” at the HF/6-31G** level and found the presence of the reverse barrier of 0.07 eV. The presence of the reverse barrier in this simple bond cleavage reaction must be due to the aromatic stabilization of the product Bz•−, just as in MC••− → Tr•+ + CH3•. Then, if PD of pXL•• proceeds solely via this pathway, one would expect a nonstatistical-looking KERD with small probability near zero kinetic energy release, in contrast with the present experimental result. Or, if PD of pXL•• proceeds via mechanism 2, its KERD is not expected to be identical to that of EB••. Hence, we conclude that PD of pXL••, and other xylene isomeric ions also, proceeds via the same mechanism as in MID.

Rate Constants. To determine the PD rate constants, we recorded the MIKE spectra, or the time-resolved PD-MIKE spectra, such that the photoexcitation and dissociation occur in the presence of an electric field. The time-resolved PD-MIKE profile for the methyl loss of EB•• at 514.5 nm recorded with the electric field of 0.5 kV/cm is shown in Figure 5a. Tailing of the main peak toward the lower translational energy direction occurs because of the time delay between photoexcitation and dissociation. The noisy feature at much lower translational energy (~6870 eV) is due to interference from the MID background. The method to determine the rate constant by analyzing the time-resolved PD-MIKE profile is well established. Briefly, the overall time-resolved PD-MIKE profile is expressed as a weighted sum of h(K,t), which is the peak shape function for the dissociation occurring at time t:

$$H(K) = \int P(t)h(K,t) \, dt$$

(8)

h(K,t) for each t was derived from the shape of the voltage-floating PD-MIKE profile. Here, K is the translational energy scale in the MIKE spectrum. The probability density for dissociation occurring at time t, P(t), may be expressed as below, assuming the random lifetime distribution and the approximately linear relation between log k and E:

$$P(t) \propto \int P(E)k(E)e^{-E/t} \, dE \propto \int P(\log k)ke^{-\alpha t} \, d \log k$$

(9)

P(E) is the internal energy distribution for the photoexcited molecular ion. When a Gaussian-type distribution of the internal energy is assumed, the following analytic expression can be used for P(\log k):

$$P(\log k) \propto \exp[-\alpha(\log k - \log k_c)^2]$$

(10)

Here, log k_c is the most probable value of log k, and \( \alpha \) is a constant related to the width of the distribution. k_c corresponds to the rate constant at the most probable internal energy of the photoexcited ion. k_c and \( \alpha \) can be determined by a regression analysis of the experimental time-resolved PD-MIKE profile. The most probable rate constant thus obtained is (1.6 ± 0.4) × 10^8 s⁻¹. We also obtained rate constants at other argon ion laser wavelengths, roughly fit the results with the RRKM calculation, and estimated the internal energy range responsible for MID based on the random lifetime assumption, shown as the shaded region in Figure 1.

The time-resolved PD-MIKE profile for the methyl loss of pXl•• at 488.0 nm is shown in Figure 5b. This looks quite different from that of EB••, even though the available energies after photoexcitation are nearly the same in the two cases. The long tail for the dissociation occurring inside the field and the significant intensity of the dissociation occurring after the parent ions exit the field region (~6870 eV) indicate that the dissociation of pXl•• occurs with a smaller rate constant than that of EB••. The best estimate of the PD rate constant for pXl•• obtained by analyzing this profile was (5 ± 3) × 10^6 s⁻¹, which is smaller than that of EB•• by a factor of ~30. We also measured the PD rate constants for ortho and meta isomers of the xylene ions at 488.0 nm, which were (7 ± 3) × 10^6 and (8 ± 3) × 10^6 s⁻¹, respectively. The fact that the PD rate constants for all three isomers of the xylene ions are nearly the same means that the rate-determining steps for these reactions occur via the same or energetically similar transition states, as was the case for reactions near the threshold (MID). These rate-determining steps can be either the XL•• → MC•• isomerization or MC•• → EB••. We could not determine experimentally which of these two steps was rate-determining because the PD experiment for MC•• could not be done. However, considering the results from the analysis of MID-KERDs, it is likely that these rate-determining steps are the isomerization to MC••. The fact that the PD rate constants for pXl•• and EB•• are different can also be explained by difference in the reaction pathways. We ruled out such a possibility based on the KERD data.

Figure 5. Time-resolved PD-MIKE profiles of C6H7•− produced from (a) the ethylbenzene ion at 514.5 nm and from (b) the p-xylene ion at 488.0 nm. Experimental and calculated results are shown as solid circles and solid curves, respectively.
The pattern of the time-resolved PD-MIKE profile for EB**+, Figure 5a, allows further reasoning on the isomerization processes in Scheme 1. If the isomerization of the photoexcited EB**+ to pXL**+ can compete with the direct dissociation to Bz**+ + CH4+, pXL**+ thus formed will dissociate slowly, with the rate constant equivalent to its own PD rate constant (∼5 × 109 s−1). Namely, pXL**+ will play the role of a kinetic trap for the excited C6H10**+. Then, the time-resolved PD-MIKE profile for pXL**+, Figure 5b, should appear overlapped on the profile in Figure 5a corresponding to faster dissociation. Near absence of the slow dissociation component in Figure 5a, even though excessive noise in the 6900−7050 eV region in this figure may be attributed to this component, means that the direct dissociation is faster than the isomerization, at least by an order of magnitude. This also allows the following interpretation of the results from the 13C scrambling study of the C6H10**+ systems performed by Grotemeyer and Grützmacher. It was suggested that scrambling of the 13C isotope incorporated in the methyl group of ethylbenzene and methylcycloheptatriene requires efficient forward and backward isomerizations between MC**+ and pXL**+ in the time scale of dissociation. In the electron ionization spectra of these two compounds, which represent high energy, namely, isomerization to MC**+ proceeds via the same mechanism found at the lower internal energy, experimental kinetic-energy release data do not support the change in the dissociation pathway to the “H ring-walk” channel. Hence, we conclude that this reaction proceeds via the same mechanism found at the lower internal energy, namely, isomerization to MC**+ and then to EB**+ followed by dissociation.

The mechanistic picture for the dissociation of the C6H10**+ system presented in this work summarized as Scheme 1 was derived from a detailed analysis of the experimental kinetic energy release distribution and the rate constant. The former was helpful to elucidate the nature of the dissociation steps, whereas the latter was helpful to gain information on the rate-determining steps. This picture is clearly in conflict with the one postulated by Grotemeyer and Grützmacher on the basis of the semiempirical calculation and the 13C labeling study. Calculation of the reaction pathways at higher levels would be useful to interpret the present experimental findings. We have not been successful in this effort yet.

A series of investigations performed in this laboratory for the production of C7H7+ from C6H5**+ (toluene**+),8 C6H10**+ (ethylbenzene**++; methylcycloheptatriene**++; and α-, m-, and p-xylene**+), and C6H8**+ (n-propylbenzene**+)10 in MID shows an interesting trend in the variation of the Bz**/Tr**+ ratio with the total number of carbon atoms in the alkyl groups attached to the ring. The percentage of Bz**+ is ∼17% for the production from C6H5**+, ∼66% from C6H10**+, and 100% from C6H7**+. Changes in the rate constants for the isomerization and dissociation steps as alkyl groups are added must be responsible for such a variation. Accurate determination of the potential-energy diagrams, especially the energies and structures of the transition states, would be needed to explain this trend.

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References and Notes

(22) NIST Standard Reference Database 69; Feb 2000: NIST chemistry WebBook.


(26) Unpublished results.


