Dissociation Dynamics of \( n \)-Propylbenzene Molecular Ion

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Production of \( \text{C}_7\text{H}_7^+ \) from \( n \)-propylbenzene molecular ion has been studied using mass-analyzed ion kinetic energy spectrometry. The kinetic energy release distributions in photodissociation and metastable ion decomposition have been determined. The photodissociation rates have been determined also on a nanosecond time scale. All the experimental data could be explained well with the microcanonical transition-state theories when the reaction was assumed to produce only the benzylium ion. Molecular orbital calculations have been carried out to understand the reason for the dominance of the benzylium channel in this system over the tropylium channel, which is important in the dissociation of smaller alkylbenzene ions.

1. Introduction

Production of \( \text{C}_7\text{H}_7^+ \) from various molecular ions has been the subject of numerous experimental and theoretical studies in the field of gas-phase ion chemistry.\(^{1-32} \) This has been investigated using a variety of methods including ordinary mass spectrometry,\(^{1,2} \) collision-induced dissociation (CID),\(^{3-6} \) ion cyclotron resonance (ICR),\(^{7-10} \) photoionization,\(^{11-13} \) multiphoton ionization,\(^{14-16} \) photoelectron–photoion coincidence (PEPICO),\(^{17-20} \) photodissociation (PD),\(^{21-24} \) and molecular orbital calculation.\(^{25-31} \) Recent studies include the determination of the absolute rate constants for the production of \( \text{C}_7\text{H}_7^+ \) from various precursor ions such as alkylbenzenes\(^{8,21,27} \) and halotoluenes\(^{6,9,13,14,25,26} \) as well as the determination of the isomeric compositions of the reaction products.\(^{4-7,10,13,16,24,26} \)

Production of \( \text{C}_7\text{H}_7^+ \) from alkylbenzene molecular ions displays an interesting trend. Among this series, dissociation of the toluene molecular ion (\( \text{C}_7\text{H}_8^+ \)), which may be considered as a prototype for the fragmentation chemistry of substituted aromatic ions, has attracted particular attention.\(^{1,5,8,10,17-19,23,24} \) Investigations over the years have shown that two isomeric ions, namely benzyl (\( \text{Bz}^+ \)) and tropylium (\( \text{Tr}^+ \)), are produced and that the isomerization of the reactant ion between toluene (\( \text{TOL}^+ \)) and cycloheptatriene (\( \text{CHT}^+ \)) structures is rapid at the threshold for the hydrogen atom loss from \( \text{C}_7\text{H}_8^+ \).

\[
\text{CH}_3^+ + \text{C}_7\text{H}_8^+ \rightarrow \text{CH}_3\text{C}_7\text{H}_7^+ + \text{H}^+ \rightarrow \text{CH}_3^+ + \text{C}_7\text{H}_7^+ + \text{H}^+ \rightarrow \text{CH}_3^+ + \text{C}_7\text{H}_7^+ \rightarrow \text{C}_7\text{H}_7^+ + \text{C}_2\text{H}_5^+ \quad (1)
\]

Even though the above scheme is widely accepted, there have appeared various contradictory claims on the details of the reaction. This is mainly because the physicochemical data obtained with various methods is seemingly contradictory. Recently, Lifshitz and co-workers\(^{17,18} \) carried out the kinetic analysis of this reaction using the molecular parameters obtained by ab initio calculations. It was shown that most of the physicochemical data could be explained by invoking the case c isomerization/dissociation mechanism of Baer\(^{33} \) and thermal energy distribution and infrared radiative decay of the reactant. Production of \( \text{C}_7\text{H}_7^+ \) from ethylbenzene molecular ion and its derivatives has been investigated also,\(^{2,5,24,28} \) even though not as extensively as production from \( \text{C}_7\text{H}_8^+ \). Isotopic labeling and other studies have shown that the rearrangement of the molecular ions with sufficient internal energy to the cycloheptatriene structure occurs rapidly in this case also.\(^{2,5} \) Among the higher alkylbenzene ions, dissociation of \( n \)-butylbenzene molecular ion has been investigated most extensively.\(^{3,11,12,21,27,29} \) Even though the emphasis of most of the studies was placed on the internal energy dependence of the \( [\text{C}_7\text{H}_7^+]/[\text{C}_7\text{H}_8^+] \) ratio, it was also found that the loss of \( \text{C}_3\text{H}_7^+ \) occurred via a simple bond cleavage and only the \( \text{C}_7\text{H}_7^+ \) isomer with the benzylium structure that was generated.\(^{12,21,27} \) The fact that the production of the tropylium ion, which may occur via an intermediate with the structure of the cycloheptatriene derivative, is not important in this case is in contrast with the cases of toluene and ethylbenzene molecular ions. Accordingly, it is of interest to study the dissociation dynamics of \( n \)-propylbenzene molecular ion, which lies between ethylbenzene and \( n \)-butylbenzene in the alkylbenzene homologue series.

In the present work, \( \text{C}_7\text{H}_7^+ \) loss of the \( n \)-propylbenzene ion has been investigated using the nanosecond photodissociation kinetics technique developed in this laboratory.

\[
n\text{C}_8\text{H}_9\text{C}_7\text{H}_7^+ \rightarrow \text{C}_7\text{H}_7^+ + \text{C}_2\text{H}_5^+ \quad (2)
\]

As will be shown later, \( \text{C}_7\text{H}_7^+ \) generated by reaction 2 has the benzylium structure as for the case of \( n \)-butylbenzene ion. One advantage in studying the dissociation of \( n \)-propylbenzene ion over that of \( n \)-butylbenzene is that the rearrangement channel leading to the production of \( \text{C}_7\text{H}_7^+ \) is not important. Reduced interference from \( \text{C}_7\text{H}_7^+ \) generated in the experimental data means that the rate constant and the kinetic energy release distribution for the production of \( \text{C}_7\text{H}_7^+ \) can be evaluated more reliably. More importantly, the smaller size of \( n \)-propylbenzene ion compared with \( n \)-butylbenzene ion allows for the determination of molecular and transition-state structures by quantum chemical calculations, even though at modest levels, which is also included in this work.
Dissociation of n-Propylbenzene Molecular Ion

2. Experimental Section

A double-focusing mass spectrometer with reverse geometry (VG analytical model ZAB-E) modified for photodissociation kinetics study was used in this work. n-Propylbenzene was introduced into the ion source via a septum inlet and was ionized by 70 eV electron ionization or by charge exchange using CS2 as the reagent gas. Ion source temperature was maintained at 180 °C in electron ionization and at 140 °C in charge exchange ionization. Ions generated were accelerated to 8 keV.

Mass-analyzed ion kinetic energy spectrometry (MIKES) was used to observe the dissociation of n-propylbenzene molecular ion. Namely, the molecular ion was separated by the magnetic sector, and the translational kinetic energy of a product ion generated in the second field-free region of the instrument was analyzed by the electric sector. Two different modes of dissociation of n-propylbenzene ion were investigated. These are the unimolecular or metastable ion decomposition (MID) and the photodissociation (PD). To generate the molecular ions for MID and PD studies, 70 eV electron ionization and charge exchange ionization were used, respectively.

The photodissociation technique developed in this laboratory for the study of ion dissociation dynamics was described in detail previously. 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 607 nm output of a dye laser (Spectra Physics model 375B), the 514.5 and 488.0 nm lines of an argon ion laser (Spectra Physics model 164-09), and the UV multiple lines (average wavelengths of 357 nm) of an argon ion laser (Spectra Physics BeamLok 2065-7s) were used. The laser beam was modulated with a chopper, and phase-sensitive detection was employed. This was to remove the background originating from MID or collision-induced dissociation (CID) by residual gas. The electrode assembly described previously has been slightly modified such that two different modes of operation are possible. In the first mode, high voltage is applied to only one of the electrodes such that the electric field is present in the dissociation region. This enables time-resolved PD study as in the original design. The new design adds the capability to float the dissociation region at high voltage. A PD-MIKE spectrum recorded under this condition, which will be called the voltage-浮动 PD-MIKE spectrum, allows the determination of the kinetic energy release distribution. With the original design, similar information was obtained by recording a field-off PD-MIKE spectrum. The fact that the interference from the MID and CID backgrounds can be significantly reduced is the advantage of the present design.

To improve the quality of PD- or MID-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.

3. Computational Section

The ab initio and semiempirical MO calculations were performed for some important geometries using the Gaussian 94 and suite of programs on CRAY-T3E LC128/128, and IBM SP2 computers. These include n-C6H5C3H7+*, Bz+, C7H7+, ethylenedioxytriphene ion (ECHT*) and intermediates. An attempt was made to find transition states connecting these structures. Special attention was paid to finding the transition state for 1,2 migration. This 1,2 migration transition state corresponds to TS 5–11 reported by Lifshitz and co-workers, which was the highest saddle point along the reaction path for TOL+* ↔ CHT+* isomerization. Geometries were optimized at the levels of MNDO, HF/3-21G, 6-31G, and 6-31G** with 4.5 × 10−4 hartree/bond convergence tolerance. Post-SCF calculation was not attempted because of the excessive computing time required for the transition-state location. TS 5–11 for TOL+* ↔ CHT+* was also calculated at the same levels. This was to compare the dissociation energetics of n-propylbenzene ion with that of toluene ion.

4. Results and Discussion

Investigations on the dissociation of n-propylbenzene ion reported so far were made mainly as an attempt to study the structure of the C6H5+ product from substituted benzene ions. No detailed study on its dissociation dynamics has been reported yet. McLoughlin et al. measured the appearance energies for the C6H5+ fragment ions from C1−C4 monosubstituted alkylbenzenes by photoionization and suggested that the production of C6H5+ with the tropyl structure at the threshold is responsible for the low values of the appearance energies measured. In their studies on reaction 1, however, Huang and Dunbar and also Ohmichi and co-workers suggested that the above results are erroneous due to the neglect of the thermal energy of the neutrals. Two CID studies by McLafferty and Winkler and by Buschek et al. suggested that the C6H5+ formed from n-propylbenzene in the ion source is a mixture of benzyl and tropyl. We attempt here to establish that the incipient C6H5+ generated from n-propylbenzene ion has the benzyl structure based on the rate—energy and kinetic energy release distribution data obtained in this work.

In the MIKES spectrum of the metastable ion decomposition (MID), or MID-MIKE spectrum, of n-propylbenzene ion obtained in this work, fragment ions C6H6++, C6H5+, C6H5++ and C6H5+ appeared with the relative abundances of 18, 44, 10, and 28%, respectively. In the photodissociation experiments, reaction 2 was found to be the dominant channel. At all the wavelengths used in the present study, the relative abundance of C6H5+ in the PD-MIKE spectra was ~90% of the total fragment ions. The other product ions, C6H6++, C6H6++, and C6H5++, appeared with the relative abundances of 3, 3, and 4%, respectively.

The molecular ion for photodissociation study was generated in the ion source by charge exchange with CS2++. When the possibility of collisional relaxation in the ion source is ignored, the internal energy of the molecular ion after photoexcitation can be estimated as follows:

\[ E = RE − IE + E_{th} + hν \]  \hspace{1cm} (3)

Here, RE is the recombination energy of CS2++ and IE is the ionization energy of n-propylbenzene. Their best literature values are 10.07 eV and 8.72 eV, respectively. E_th is the thermal internal energy at 140 °C. Its distribution was calculated with the molecular parameters in Table 3 according to the well-established method. The most probable internal energies of the n-propylbenzene ions thus estimated are 3.63, 4.00, 4.13, and 5.06 eV, respectively, for photodissociation at 607, 514.5, 488.0, and 357 nm. Collisional relaxation in the source was found not to be important for the determination of the kinetic energy release distribution, while a proper correction had to be made for the determination of the rate constant (to be described later). The internal energy of the molecular ion undergoing MID cannot be determined experimentally. Hence, it was estimated from the theoretical rate—energy relation (to be presented later) as follows. The average total rate constant for MID of 3.4 × 10^8 s⁻¹ was estimated from the parent ion transit time (τ = 29
the production of \( \text{Bz}^+ \) structure, resulted in an average KER of 0.32 eV, 39 respectively. The average KERs in PD at other wavelengths were also measured. They are all listed in Table 1.

**Kinetic Energy Release Distribution (KERD).** MIKE profiles of \( \text{C}_7\text{H}_7^+ \) generated in MID and PD at 488.0 nm are shown in Figure 1. These profiles were recorded with the dissociation region floated at high voltage as was described in a previous section. The method to evaluate KERD from such MIKE profiles was reported previously.\(^{38}\) The contamination-free halves of the profiles were used to evaluate KERDs. The results are shown in Figure 2. The average values of the kinetic energy release (KER) were evaluated from the distributions. These were 0.054 and 0.125 eV for MID and PD at 488.0 nm, respectively. The average KERs in PD at other wavelengths were also measured. They are all listed in Table 1.

It is well-known that a large reverse barrier is present in the \( \text{CH}_2\text{H}_7^+ \rightarrow \text{Tr}^+ + \text{H}^+ \) reaction,\(^{17,18,31}\) which leads to a large average KER. Our own measurement for MID of \( \text{TOL}^+ \) at 488.0 nm 5.06 \( \pm \) 0.185 eV.\(^{37}\) which is 6 times larger than the corresponding value for \( \text{C}_2\text{H}_5^+ \). Then, the internal energy of the parent ion corresponding to the above average rate constant was read from the rate—energy curve. This turned out to be 2.30 eV for MID, occurring near the intermediate focal point of the instrument.

**Figure 1.** MIKE spectra for \( \text{C}_2\text{H}_5^+ \) loss from \( n\)-propylbenzene ion: (a) MID-MIKE spectrum obtained with the electrode assembly floated at \( -1.5 \) kV; (b) PD-MIKE spectrum at 488.0 nm excitation obtained with the electrode assembly floated at 1.5 kV.

\( \pm 2 \mu \text{s} \). The branching ratio of \( \text{C}_7\text{H}_7^+ \) in the MID-MIKE spectrum was multiplied by the above to obtain the average rate constant for the production of \( \text{C}_7\text{H}_7^+ \). Then, the internal energy of the parent ion corresponding to the above average rate constant was read from the rate—energy curve. This turned out to be 2.30 eV for MID, occurring near the intermediate focal point of the instrument.

**Figure 2.** Kinetic energy release distributions for \( \text{C}_2\text{H}_5^+ \) loss from \( n\)-propylbenzene ion: (a) MID and (b) PD at 488.0 nm. Experimental results are shown as filled circles. Theoretical results (phase space theory) are shown as solid curves. Bars represent error limits.

**Table 1: Kinetic Energy Releases and Rate Constants for Reaction 2**

<table>
<thead>
<tr>
<th>Internal energy (eV)</th>
<th>KER (eV)</th>
<th>Rate constant ( (\text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>607 nm</td>
<td>3.63</td>
<td>0.054 ( \pm 0.004 )</td>
</tr>
<tr>
<td>514.5 nm</td>
<td>4.00</td>
<td>0.122 ( \pm 0.012 )</td>
</tr>
<tr>
<td>488.0 nm</td>
<td>4.13</td>
<td>0.125 ( \pm 0.013 )</td>
</tr>
<tr>
<td>357 nm</td>
<td>5.06</td>
<td>0.185 ( \pm 0.020 )</td>
</tr>
</tbody>
</table>

\(^{a}\) Estimated from the rate—energy curve obtained in the photodissociation study. \(^{b}\) Estimated from the parent ion transit time. \(^{c}\) Not determined due to poor signal quality.

\[ n(T,J,E) \propto \int_{R_m}^{E-E_0-T} \rho(E-E_0-T-R)P(T,J,R) \, dR \quad (4) \]

Here, \( n(T,J,E) \) is the KERD at the angular momentum \( J \) and the internal energy \( E \). The root-mean-square average \( J \) value evaluated at the ion source temperature has been used. \( \rho \) and \( P \) are the product vibrational and angular momentum state densities, respectively. \( R \) is the product rotational energy and \( R_m \) is its minimum. \( E_0 \) is the reaction critical energy, which may be set equal to the reaction endoergicity at 0 K under the assumption of a completely loose transition state. The value of \( E_0 \) evaluated from the best literature thermochemical data,\(^{37,41-43}\) listed in Table 2, is 1.73 eV. The method to estimate the internal energy \( E \) has been presented already. In the case of photodissociation, KERD has been calculated at various internal energies and averaged over the internal energy distribution. Molecular parameters obtained at the HF/6-31G** level (vide infra) were used in the calculation. These are listed in Table 3.

KERDs calculated for MID and PD at 488.0 nm are compared with the experimental data in Figure 2. The agreement between the experimental and theoretical KERDs is excellent, as is seen...
TABLE 2: Thermochemical Data

<table>
<thead>
<tr>
<th>species (structure)</th>
<th>( \Delta H_{298}^f ) (kJ mol(^{-1}))</th>
<th>( \Delta H_{10K}^f ) (kJ mol(^{-1}))</th>
<th>IE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n-C_7H_7C_7H_7 )</td>
<td>7.9(^b)</td>
<td>44.8</td>
<td>8.72(^b)</td>
</tr>
<tr>
<td>( n-C_7H_7C_7H_7^+ )</td>
<td>849(^b)</td>
<td>886</td>
<td></td>
</tr>
<tr>
<td>( C_6H_6CH_3+ ) (benzyl)</td>
<td>907(^c)</td>
<td>926 (\dagger)</td>
<td></td>
</tr>
<tr>
<td>( C_6H_6^+ )</td>
<td>116.3 (\dagger)</td>
<td>126.9</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Estimated from 298 K data as described in ref. 41. \(^b\) Taken from ref. 37. \(^\dagger\) Taken from ref. 38. \(^\ddagger\) Taken from ref. 43.

in the figures. Excellent agreement was also achieved for PD at 357 and 514.5 nm. Upon recollection that the production of Tr\(^+\) would accompany a significant kinetic energy release, it seems safe to conclude that the incipient C\(_7\)H\(_7^+\) ion generated by reaction 2 has mostly the benzyl structure.

It is to be mentioned that the above conclusion does not mean that C\(_7\)H\(_7^+\) generated by electron ionization of \( n \)-propylbenzene in the ion source has the benzyl structure also. This is because the benzylion ion generated with a sufficient internal energy may undergo isomerization to the tropyl structure. The energy barrier for such an isomerization was estimated to be 137 kJ mol\(^{-1}\) (1.42 eV) in the MINDO/3 study reported by Cone et al.\(^{31}\) Then, the Bz\(^+\) \( \rightarrow \) Tr\(^+\) isomerization may also occur for Bz\(^+\) produced by photodissociation in this study. It is to be noted, however, that such an isomerization does not affect the kinetic energy of C\(_7\)H\(_7^+\).

**Rate–Energy Relation.** The PD-MIKE profile for reaction 2 at 514.5 nm obtained with 1.5 kV applied on one of the electrodes in the electrode assembly is shown in Figure 3. The lower energy tail of this profile, which is called the field-on PD-MIKE profile, occurs due to the time delay between photoexcitation and dissociation. The method to obtain the rate constant or its distribution from such a profile was described in detail previously.\(^{44}\) Briefly, the overall field-on 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 \( t \).

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

\( h(K,t) \) for each \( t \) was derived from the shape of the voltage-floated 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 \( E \).

\[
P(t) \propto \int P(E)k(E)e^{-kE} \, dE \propto \int P(\log k)ke^{-k} \, d \log k
\]

\( P(E) \) 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 \( P(\log k) \).

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

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 field-on PD-MIKE profile. In the case of the profile shown in Figure 3, the best \( k_c \) and \( \alpha \) values were 2.6 \( \times \) 10\(^8\) s\(^{-1}\) and 6.8, respectively. In our previous photodissociation studies,\(^{26,27,44}\) the collisional relaxation occurring in the ion source was found to affect the internal energy of the molecular ion and an experimental technique to correct for the relaxation was developed. Following the same procedure, the collisional relaxation-free \( k_c \) was estimated by extrapolating the high-pressure data to the zero-pressure limit in this work. The rate constant thus obtained corresponds to the sum of the rate constants for all the competing dissociation channels of the molecular ion. The field-on PD-MIKE profiles of other fragments such as C\(_6\)H\(_6^+\), and C\(_7\)H\(_6^+\) were also asymmetrical, even though their quality was not good enough for the determination of the rate constant. Instead of the direct analysis, their field-on PD-MIKE profiles were calculated with the rate constants determined from the C\(_7\)H\(_7^+\) profiles. A good agreement between the experimental and calculated profiles was achieved, which was taken as the evidence for the competitive production of all the fragment ions. Then, the rate constant for reaction 2 was estimated by multiplying the C\(_7\)H\(_7^+\) branching ratio by the total rate constant. The photodissociation rate constants for reaction 2 thus obtained are listed in Table 1. For photodissociation at 357 nm the field-on PD-MIKE profile was symmetrical. This means that the dissociation occurs faster than the time resolution of the present technique. The maximum rate constant that can be determined with the present method is estimated to be 8 \( \times \) 10\(^8\) s\(^{-1}\).

To interpret the experimental rate–energy data, RRKM-QET calculation of the rate constant has been carried out.

\[
k(E) = \frac{W^\Phi(E-E_0)}{\hbar \rho(E)}
\]

Here, \( \rho \) is the density of states of the reactants, \( W^\Phi \) is the state sum at the transition state, and \( \sigma \) is the reaction path degeneracy. Since the difference in the external rotational moments of inertia between the reactant and the transition state is generally ignored, the rotational energy has not been included in the estimation of the reactant internal energy. In a usual RRKM-QET fitting of rate–energy data, the critical energy and the activation entropy at 1000 K (\( \Delta S^0 \)) is treated as two adjustable parameters. In the present case, \( E_0 \) was fixed at 1.73 eV, which is the value used in the calculation of KERD and only \( \Delta S^0 \) was adjusted to fit the experimental data. The best fit was achieved with a \( \Delta S^0 \) of 35.2 J mol\(^{-1}\) K\(^{-1}\) as shown in Figure 4. The vibrational frequencies used for the calculation are listed in Table 3. A C–C stretching mode at 1061 cm\(^{-1}\) was taken as the reaction coordinate. The calculated rate constant corresponding to photodissociation at 357 nm is 5.0 \( \times \) 10\(^8\) s\(^{-1}\), which is larger than the maximum rate constant (8 \( \times \) 10\(^8\) s\(^{-1}\)) that can be determined with the present method. This agrees with the observation of the symmetrical shape of the field-on PD-MIKE profile at this wavelength.

\( \Delta S^0 \) of 35.2 J mol\(^{-1}\) K\(^{-1}\) (\( = 8.42 \) cal mol\(^{-1}\) K\(^{-1}\)) indicates that the reaction occurs via a loose transition state. This is in agreement with the simple bond cleavage to the benzylion structure as was concluded in the analysis of KERD. \( E_0 \) and \( \Delta S^0 \) determined here are similar to those (\( E_0 = 1.61 \) eV, \( \Delta S^0 = 7.28 \) cal mol\(^{-1}\) K\(^{-1}\)) obtained for the production of C\(_7\)H\(_7^+\) from \( n \)-butylbenzene ion.\(^{27}\) It is to be mentioned that the kinetic analysis for the latter reaction led to the conclusion that the C\(_7\)H\(_7^+\) generated had benzyl structure. The magnitudes of \( E_0 \) and \( \Delta S^0 \) determined in this work may not be so accurate because the experimental rate–energy data are available over a limited time range. Further experimental studies on extended time scales are needed to refine the kinetic parameters.

**Molecular Orbital Calculations.** Minimum-energy geometries (Figure 5) and energies and vibrational frequencies at these geometries for \( n \)-propylbenzene ion (NPB\(^+\)), Bz\(^+\), and C\(_7\)H\(_6^+\)
TABLE 3: Molecular Parameters Used in the Calculations of Rate Constants, KERDs, and Internal Energy Distribution

<table>
<thead>
<tr>
<th>Vibrational Frequencies (cm⁻¹)</th>
<th>Rotational Constants (cm⁻¹)</th>
<th>Polarizability (10⁻24 cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3059 3055 3042 3039 2954 2951 2942 2915 2899 2880 2876 1601 1491 1476 1463 1461 1457 1419 1400 1362 1337 1324 1290 1280 1257 1201 1173 1164 1117 1046 1005 1002</td>
<td>0.139 0.179 3.51</td>
<td>6.22</td>
</tr>
<tr>
<td>3059 3055 3042 3039 2954 2951 2942 2915 2899 2880 2876 1601 1491 1476 1463 1461 1457 1419 1400 1362 1337 1324 1290 1280 1257 1201 1173 1164 1117 1046 1005 1002</td>
<td>0.0292 0.0945 0.753</td>
<td>0.0620</td>
</tr>
<tr>
<td>3059 3055 3042 3039 2954 2951 2942 2915 2899 2880 2876 1601 1491 1476 1463 1461 1457 1419 1400 1362 1337 1324 1290 1280 1257 1201 1173 1164 1117 1046 1005 1002</td>
<td>0.179 0.0620</td>
<td>0.699</td>
</tr>
<tr>
<td>3059 3055 3042 3039 2954 2951 2942 2915 2899 2880 2876 1601 1491 1476 1463 1461 1457 1419 1400 1362 1337 1324 1290 1280 1257 1201 1173 1164 1117 1046 1005 1002</td>
<td>0.0292 0.0620</td>
<td>0.699</td>
</tr>
</tbody>
</table>

The HF/6-31G* results multiplied by 0.90. Estimated value. See text for the definition. The HF/6-31G** results for the MNDO geometry multiplied by 0.90. The HF/6-31G** results.

Figure 3. PD-MIKE spectrum at 514.5 nm for C₂H₅ loss from n-propylbenzene ion obtained with 1.5 kV applied on one of the electrodes in the electrode assembly. Experimental and calculated results are shown as filled circles and a solid curve, respectively. A slight discrepancy between the two results at the high translational energy side is due to the production of C₃H₄⁺.

These were calculated. Attempts were made at various calculation levels to obtain the potential energy curve between NPB⁺ and the ethylcycloheptatriene (ECHT⁺) structure and between ECHT⁺ and Tr⁺ + C₃H₄⁺. Saddle points were located, and the intrinsic reaction coordinates (IRCs) were calculated to confirm that a particular saddle point found was connected to the reactant, product, or intermediates. Such an effort was partially successful at the MNDO level, and the reaction to Tr⁺ and Bz⁺ is presumed to occur via the following mechanism.

Figure 4. Rate-energy dependence for C₃H₄⁺ loss from n-propylbenzene ion. Experimental results are shown as filled circles. The result for the photodissociation at 357 nm is shown as an arrow. The theoretical result (RRKM-QET) is shown as the solid curve. Rate parameters used in the calculation are E₀ = 1.72 eV and ΔS₀ = 35.2 J mol⁻¹ K⁻¹ (8.42 cal mol⁻¹ K⁻¹). Bars represent error limits. The dashed curve is a rough RRKM-QET estimate of the rate-energy dependence for the isomerization to ECHT⁺ calculated with E₀ = 1.72 eV and the vibrational frequencies for NPB⁺ and TS 5⁻→11⁻ in Table 3.

Structures of the intermediate 11⁻ and the saddle point TS 10⁻→6 could not be determined due to the computational difficulty. Notations for the stable structures and the transition states have been taken from Dewar and Landman.17 The saddle point 5⁻→11⁻ is equivalent to TS 5⁻→11 in the TOL⁺→ECHT⁺ isomerization reported by Lifshitz and co-workers.17 Similar saddle points, namely TS 5⁻→11⁻, could be found at Hartree–Fock levels (Figure 6). To confirm that these are the transition-state structures for the NPB⁺→ECHT⁺ isomerization, the intrinsic reaction coordinates (IRCs) were calculated also. It was found that these structures led to the NPB⁺ structure via the backward reaction. The forward IRC calculations in the Hartree–Fock levels were not successful, however, due to the presence of tiny local minima near the saddle points. Namely, these saddle points may not be the true transition states even though their structures look similar to the one found at the MNDO level. Then, the energies at the true transition state
may be higher than those of the above saddle points. The Hartree–Fock calculations were also done for the MNDO transition-state geometry. At a given HF level, the energy difference between the saddle point found at this level and the MNDO transition-state structure was around 0.1 eV. The zero-point energy correction was made for the minimum-energy and saddle-point geometries. The usual 10% correction for the vibrational frequencies was made for the HF level calculations, while the correction factors reported by Dewar and co-workers48 were utilized for the MNDO results. Then, the critical energy for the production of Bz$^+$ ($E_d(\text{NPB}^+ \rightarrow \text{Bz}^+)$) was evaluated as the difference between the energies of Bz$^+$ + C$_2$H$_5^*$ and NPB$^+$. The critical energy for the isomerization to ECHT$^+$, $E_d(\text{NPB}^+ \rightarrow \text{ECHT}^+)$, was evaluated using two different estimates of the transition-state energy, the one obtained at the saddle point found at that ab initio level and the other obtained by the ab initio calculation for the MNDO transition-state geometry. Similar calculations were performed for the corresponding reactions of TOL$^+$ for comparison. In the case of TOL$^+$, there was no ambiguity in the determination of the transition state for the isomerization. The four critical energies, $E_d(\text{NPB}^+ \rightarrow \text{Bz}^+)$, $E_d(\text{NPB}^+ \rightarrow \text{ECHT}^+)$, $E_d(\text{TOL}^+ \rightarrow \text{Bz}^+)$, and $E_d(\text{TOL}^+ \rightarrow \text{CHT}^+)$, thus obtained are listed in Table 4.

It is seen that the critical energy for the production of Bz$^+$ from TOL$^+$ is consistently higher than the isomerization barrier to CHT$^+$. This is in qualitative agreement with the results of Lifshitz and co-workers.17 Even though there is some uncertainty in the evaluation of the isomerization barrier in the case of NPB$^+$, it is higher than the critical energy for the production of Bz$^+$ at most of the levels of calculation with the exception of the MNDO transition-state geometry. Namely, the simple bond cleavage to Bz$^+$ seems to be energetically more favorable than or comparable to the rearrangement to ECHT$^+$ in the case of n-propylbenzene ion.

A schematic potential-energy diagram for the production of Bz$^+$ from TOL$^+$ and Tr$^+$ from NPB$^+$ is shown in Figure 7. Energies of NPB$^+$, Bz$^+$, ECHT$^+$, Tr$^+$, C$_2$H$_5^*$, the intermediate 10, and the transition state between ECHT$^+$ and Tr$^+$ + C$_2$H$_5^*$ are those calculated at the HF/6-31G** level. Energies of TS 5–11 and TS 11–10 are those calculated at the HF/6-31G** level for the transition-state geometries found at the MNDO level. It is to be noted that the energy of TS 5–11 in this diagram is slightly lower than that of Bz$^+$ + C$_2$H$_5^*$, while the opposite is the case at other calculation levels.

It is well-known that in the competition between a simple bond cleavage and a rearrangement, the former becomes more favorable as the reactant internal energy increases. Then, the formation of Bz$^+$ can be preferred to that of isomerization to ECHT$^+$ in the present case, in agreement with the experimental results. To confirm this, a simple RRKM-QET calculation of the rate–energy relation for the isomerization to ECHT$^+$ has been carried out. Calculation has been done utilizing the

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**Table 4: Critical Energies (in eV) for the Production of Bz$^+$ and the Isomerization to the Cycloheptatriene Structure from Toluene and n-Propylbenzene Ions Calculated at Various Levels**

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>MNDO</th>
<th>HF/3-21G</th>
<th>HF/6-31G</th>
<th>HF/6-31G**</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_d($TOL$^+ \rightarrow$ Bz$^+$)</td>
<td>2.30</td>
<td>2.12</td>
<td>2.10</td>
<td>2.23</td>
</tr>
<tr>
<td>$E_d($TOL$^+ \rightarrow$ ECHT$^+$)</td>
<td>1.82</td>
<td>1.91</td>
<td>1.92</td>
<td>1.93</td>
</tr>
<tr>
<td>$E_d($NPB$^+ \rightarrow$ Bz$^+$)</td>
<td>0.94</td>
<td>1.49</td>
<td>1.30</td>
<td>1.48</td>
</tr>
<tr>
<td>$E_d($NPB$^+ \rightarrow$ ECHT$^+$)</td>
<td>1.45</td>
<td>1.55</td>
<td>1.55</td>
<td>1.57</td>
</tr>
</tbody>
</table>

*Calculated using the energy of the saddle point obtained at this level. 'Calculated using the energy of the MNDO transition-state structure obtained at this level. $^2$ Estimated with the thermochemical data for reactants and products in Table 2 and ref 37.

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**Figure 7.** Schematic potential-energy diagram for C$_2$H$_5^*$ loss from n-propylbenzene ion. Notations for the structures follow those by Dewar and Landman.47 The boldface numbers denote the energy in kJ mol$^{-1}$ referred to the energy minimum of NPB$^+$.

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**Figure 5.** Minimum-energy geometries for n-propylbenzene ion (NPB$^+$), Bz$^+$, and C$_2$H$_5^*$ calculated at the HF/6-31G** level.

**Figure 6.** Structures at the saddle point located between NPB$^+$ and the ethylcycloheptatriene (ECHT$^+$) found at various levels (a) MNDO, (b) HF/3-21G, (c) 6-31G, and (d) 6-31G**, respectively.
transition-state property evaluated at the HF/6-31G** level for the MNDO structure. The calculated critical energy for the isomerization is smaller by 1 kJ mol⁻¹ than the corresponding value for the benzyl channel. Since the critical energy of 1.73 eV was adopted for the RRKM calculation of the latter channel, 1.72 eV has been taken as the critical energy for the isomerization channel. Vibrational frequencies of the transition state calculated at the HF/6-31G** level for the MNDO structure have been used after 10% correction. These are listed in Table 3. The rate–energy relation for the isomerization thus calculated is compared with that for the production of Bz⁺ in Figure 4. It is seen that the rate constant for the production of Bz⁺ is larger than that for the isomerization by more than 2 orders of magnitude over the reactant internal energy range of 2.3–5.1 eV covered in the present work.

5. Conclusion

Dissociation dynamics of n-propylbenzene ion to C₂H₇⁺ has been investigated by the metastable ion decomposition and photodissociation methods. Comparison of the experimental KERDs with those calculated with the statistical phase space theory has shown that the incipient C₂H₇⁺ ion has the benzyl structure over the reactant internal energy range of 2.3–5.1 eV investigated in this work. The fact that KERD in the production of benzyl ion can be predicted accurately by the phase space theory suggests that KERD can play an important role in the structural determination of C₂H₇⁺ ions generated from benzene derivative ions. The rate–energy relation on the nanosecond time scale determined by the photodissociation kinetics technique also supported the production of the benzyl ion. This does not mean, however, that the benzyl structure will be retained after a prolonged time. This is because the benzylum-to-tropylium isomerization may occur for the benzyl ion generated with a sufficient internal energy.

The result from the present investigation establishes an interesting trend in the production of C₂H₇⁺ from n-alkylbenzene ions. Namely, the simple bond cleavage to Bz⁺ is the dominant channel in the dissociation of n-propylbenzene and n-butylbenzene ions. On the other hand, the isomerization to the cycloheptatriene structure and subsequent dissociation to the tropylium ion are important for toluene and ethylbenzene ions. Molecular orbital calculations carried out at the limited level of accuracy suggest that the relative heights of the barriers to the simple bond cleavage and isomerization are responsible for the above experimental trend. Quantum chemical study of the toluene and ethylene ion systems at high ab initio levels will be useful for a better understanding of the C₂H₇⁺ production mechanism. Also useful will be the measurement and/or prediction of KERD in the production of Tr⁺ from CHT⁺. These being attempted as a continuation of the present study.

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References and Notes