

Product-Resolved Photodissociations of Iodotoluene Radical Cations[§]

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Photodissociations of *o*-, *m*-, and *p*-iodotoluene radical cations were investigated by using Fourier-transform ion cyclotron resonance (FT-ICR) spectrometry. Iodotoluene radical cations were prepared in an ICR cell by a photoionization charge-transfer method. The time-resolved one-photon dissociation spectra were obtained at 532 nm and the identities of C₇H₇⁺ products were determined by examining their bimolecular reactivities toward toluene-*d*₈. The two-photon dissociation spectra were also recorded in the wavelength range 615–670 nm. The laser power dependence, the temporal variation, and the identities of C₇H₇⁺ were examined at 640 nm. The mechanism of unimolecular dissociation of iodotoluene radical cations is elucidated: the lowest barrier rearrangement channel leads exclusively to the formation of the benzyl cation, whereas the direct C–I cleavage channel yields the tolyl cations that rearrange to both benzyl and tropylium cations with dissimilar branching ratios among *o*-, *m*-, and *p*-isomers. With a two-photon energy of 3.87 eV at 640 nm, the direct C–I cleavage channel results in the product branching ratio, [tropylium cation]/[benzyl cation], in descending order, 0.16 for *meta* > 0.09 for *ortho* > 0.05 for *para*.

Keywords : FT-ICR, Time-resolved photodissociation, Iodotoluene, Tolylyl cation, Product-resolved photodissociation.

Introduction

Unimolecular dissociations of iodotoluene radical cations^{1–11} have attracted much experimental interest for the elucidation of the mechanism of C₇H₇⁺ formation.^{12–14} Iodotoluene radical cations with a few eV internal energies dissociate to C₇H₇⁺ with a loss of iodine. A number of studies have focused on the dissociation kinetics^{1–5} as well as the structures^{1,6–9} of C₇H₇⁺ from electron impact (EI) or chemical ionization of iodotoluenes. The two-channel picture currently accepted for these dissociations is as follows: The direct C–I bond cleavage, denoted channel I, produces tolyl cations,³ whereas the lowest barrier rearrangement, denoted channel II, yields the benzyl cation.¹⁴ Thermochemical thresholds for channel I, estimated from the recommended values for heats of formation of tolyl cations,¹⁵ are 2.11, 2.24, and 2.41 eV for *o*-, *m*-, and *p*-iodotoluene radical cations, respectively. The activation barriers for channel II are determined to be 1.77, 1.88, and 1.90 eV for *o*-, *m*-, and *p*-isomers, respectively.¹⁶

In spite of a wealth of information about the kinetics and energetics of the system, the propensity of isomerization of tolyl cations to the benzyl cation and/or to the tropylium cation has not been well established. All the previous structural studies did not separate partial contributions from each channel.^{1,6–9} In this work, we have differentiated the two competing dissociation channels by energy-selective excitation

of the iodotoluene radical cations and studied the structures of C₇H₇⁺ by ion-molecule reactions with toluene-*d*₈. The one-photon dissociation (1PD) at 532 nm leads to channel II only for both *m*- and *p*-isomers, whereas the two-photon dissociation (2PD) at 640 nm selects channel I predominantly for the *o*-isomer. The propensity of isomerization of tolyl cations were assessed by comparing the product branching ratios, [tropylium cation]/[benzyl cation], obtained from this work with the channel branching ratios, [channel I]/[channel II], reported elsewhere.¹⁶

Experimental Section

Our FT-ICR setup for the studies of time-resolved photodissociation (TRPD) spectroscopy and bimolecular reactivity was previously described in detail.^{13,14}

In brief, the iodotoluene radical cations were prepared in the ICR cell by a photoionization-charge-transfer (PICT) method.¹³ First, C₆D₅CD₃⁺ was produced from two-photon ionization (2PI) of toluene-*d*₈ by the 266-nm output of a Nd:YAG laser. A 3-mm diameter laser beam was used unfocused with a laser power of ~2 mJ/pulse. Because the ionization potential (IP) of toluene, 8.83 eV,¹⁷ is greater than the IPs of iodotoluenes, 8.58, 8.56, and 8.43 eV for *o*-, *m*-, and *p*-isomers,¹ respectively, exothermic charge-transfer (CT) reactions of C₆D₅CD₃⁺ with iodotoluenes yielded iodotoluene radical cations. The parent ions then underwent both radiative relaxation and thermal charge-exchange collisions with parent neutrals for 2 s before photolysis. Thus, the PICT process rapidly prepares thermalized parent ions at the

[§]This paper is dedicated to K.H. Jung on the occasion of his retirement.

housing temperature (20 °C).¹³ The parent ions were then optically excited by the 532-nm output of another Nd:YAG laser or by a tunable dye laser with the output in the wavelength range of 615-675 nm with DCM dye pumped by the Nd:YAG laser. The photolysis laser beam was 2 mm in diameter and the laser power was 1-3 mJ/pulse for 1PD at 532 nm and ~10 mJ/pulse for multiphoton dissociations in the 615-670 nm wavelength range. The rapid internal conversion transformed the deposited photon energy into the internal energy, which resulted in vibrationally hot ions. The temporal appearance of $C_7H_7^+$ was monitored by scanning a 20- μ s ICR detection burst on resonance with the ICR frequency of $C_7H_7^+$. The precise timing of photolysis pulse with respect to the ICR detection pulse was monitored by a fast photodiode. The structures of $C_7H_7^+$ from 1PD at 532 nm and 2PD at 640 nm were identified from their bimolecular reactivities toward toluene- d_8 . A 20-s reaction time was allowed after photolysis to ensure the completion of ion-molecule reactions.

All chemicals were purchased from Aldrich Inc. and used after several freeze-pump-thaw cycles. The background pressure was below 9.0×10^{-10} torr. Gaseous iodotoluene and toluene- d_8 were guided separately into the ICR cell and their partial pressures were kept at a constant ratio of 2:1 in the 10^{-8} torr range, respectively.

Results and Discussion

One-photon dissociation at 532 nm. Photodissociations of *o*-, *m*-, and *p*-iodotoluene radical cations were examined at 532 nm. Figure 1 shows the TRPD spectra. All three isomers show non-zero intercepts at $t=0$. The intercept increases with the laser power, indicating that the product ion signals within the first 20 μ s result from multi-photon processes. Thus, the laser power was adjusted in such a way to make the 1PD dominant. The TRPD signals were analyzed by using the ICR signal equation convoluted with a truncated Boltzmann distribution for the internal energy of the parent ion.¹³ The average rate constant was derived

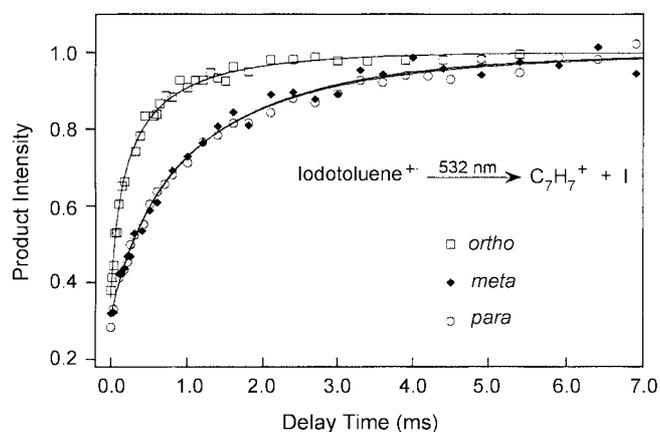


Figure 1. TRPD spectra of iodotoluene radical cations at 532 nm. The solid lines represent the best-fit curves to the convoluted ICR signal equation.

Table 1. The dissociation rate constants of the *p*-iodotoluene radical cation as a function of time delay from EI

time delay (s)	E_{thermal} (eV)	Temperature	k (s^{-1})
0.05	0.33 ± 0.03	480 ± 20	3.2×10^4
0.5	0.30 ± 0.01	460 ± 10	2.2×10^4
1.0	0.27 ± 0.01	440 ± 10	1.5×10^4
3.0	0.25 ± 0.01	425 ± 10	1.2×10^4

therefrom. The solid lines drawn in Figure 1 represent the best-fit curves using the convoluted ICR signal equation. The average rate constants for 1PD at 532 nm at 293 K are $4,300 \pm 300$, 890 ± 60 , and 850 ± 100 s^{-1} for *o*-, *m*-, and *p*-iodotoluene radical cations, respectively. They are comparable to the previously reported values of 7,356, 1,775, and 1,150 s^{-1} for *o*-, *m*-, and *p*-isomers at 375 K, respectively, by Dunbar and co-workers.^{2,3} The two independent measurements show the descending order of rate in going from *ortho* to *para*, however, there is discrepancy in the order of magnitude. Our values are smaller than the previous experiments. We ascribe the discrepancy to the difference in ion temperature between the two experiments. To test the effect of electron impact (EI) on the ion temperature, we carried out TRPD thermometry experiments with the *p*-isomer. The ion temperature was determined from the rate-energy curve as a function of time delay from a 16-eV electron beam pulse. Results are summarized in Table 1. The 1PD rate decreases with time and reaches a steady state. This result confirms that EI produces vibrationally hot ions that undergo radiative relaxation, but the radiative heating by hot filament keeps the ion temperature modestly high.¹³ The ion temperature was ~425 K, even after 3 s delay from EI.

Photodissociation in the 615-670 nm wavelength range. The PD yield spectra were obtained in the 615-670 nm wavelength range and plotted in Figure 2. Both *o*- and *p*-isomers exhibit almost identical appearance thresholds at ~670 nm, while the *m*-isomer shows a significant PD signal at 670 nm. These thresholds imply that there are optically bright excited states accessible by one-photon around 1.85 eV for all three isomers. The present spectra are in good agreement with the PD spectra reported by Dunbar and co-workers with photodissociation onsets of 1.8 eV for all three

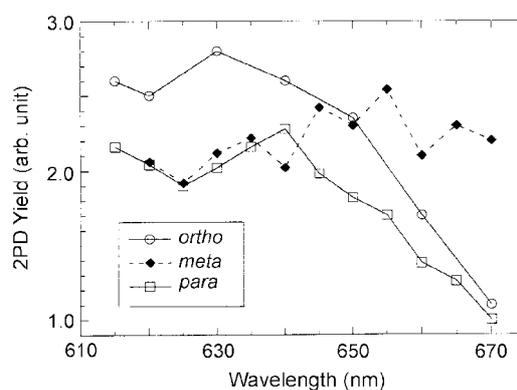


Figure 2. Two-photon yield spectra of iodotoluene radical cations.

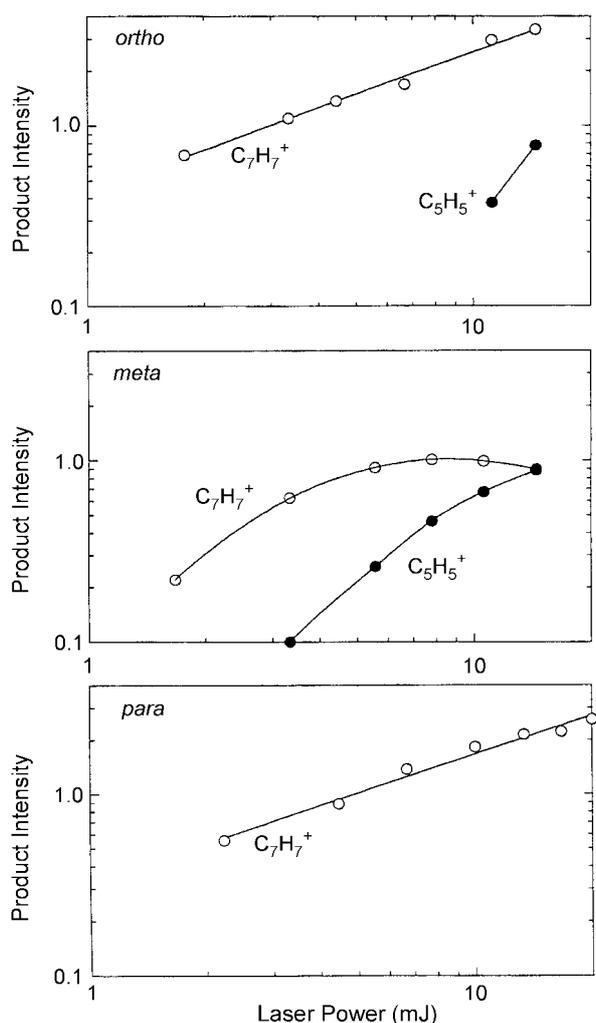


Figure 3. The laser power dependence of photodissociations of iodotoluene radical cations at 640 nm.

isomers.^{14,15} The laser power dependence was examined at 640 nm, where all three isomers display comparable PD yields as shown in Figure 2. Results are shown in Figure 3. All three isomers reveal almost identical slopes of 0.7–0.8 for the total product ion intensity as a function of laser power. These slopes suggest the saturation of one-photon absorption. As the laser power increases, $C_5H_5^+$ appears in addition to $C_7H_7^+$, however, their yields vary with isomers: $C_5H_5^+$ starts appearing from the *o*-, and *m*-isomers at ~ 11 and ~ 3 mJ/pulse, respectively, but no $C_5H_5^+$ appears from the *p*-isomer even at 20 mJ/pulse. The temporal appearance of $C_7H_7^+$ was examined at 640 nm with low laser power. Figure 4 shows the appearance curve from the *p*-isomer. All $C_7H_7^+$ products appeared within the first 20 μ s, suggesting the PD rate greater than $\sim 10^5$ s⁻¹. Other isomers exhibited almost identical appearance curves as that of the *p*-isomer. Because one-photon energy of 1.94 eV at 640 nm is just above the channel II activation barrier of 1.90 eV for the *p*-isomer, the 1PD rate is expected to be much less than 100 s⁻¹. On the other hand, the 2PD rate with a 3.87-eV internal energy is expected to be in the range of 10^6 – 10^7 s⁻¹ for the *p*-

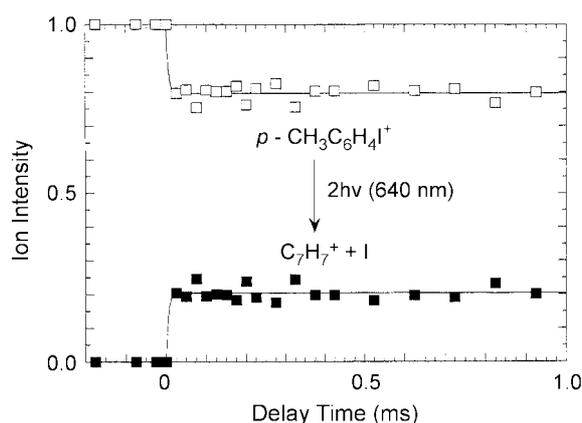


Figure 4. TRPD spectra of the *p*-iodotoluene radical cation at 640 nm.

isomer. Thus, the $C_7H_7^+$ signal within the first 20 μ s must result from at least two-photon process. The subsequent $C_5H_5^+$ signal at high laser power is presumably derived from the sequential dissociation of the iodotoluene radical cations via $C_7H_7^+$. If $C_5H_5^+$ were the vinylcyclopropenyl cation as suggested by Freiser *et al.*,¹⁸ thermochemical thresholds to give $C_5H_5^+ + C_2H_2 + I$ would be 3.65, 3.81, and 3.78 eV for the *o*-, *m*-, and *p*-iodotoluene radical cations, respectively. Because the two-photon energy of 3.87 eV at 640 nm barely meets these thresholds, the formation of $C_5H_5^+$ by two-photon absorption does not kinetically compete with that of $C_7H_7^+$ having the rate of 10^6 – 10^7 s⁻¹. To produce an appreciable amount of $C_5H_5^+$ as shown in Figure 3 at high laser power, at least three photon processes should take place. Therefore, we conclude that the $C_5H_5^+$ signal is indicative of three-photon process, while the $C_7H_7^+$ signal in the absence of $C_5H_5^+$ results mainly from two-photon process. The difference in the laser power dependence of product spectra among three isomers may be related to the difference in the rate of internal conversion that affects the overall rate of two-photon absorption.

Structures of $C_7H_7^+$ products. In 532-nm photolysis, the $C_7H_7^+$ products formed within the first 20 μ s were ejected out by applying an ejection radio-frequency pulse at 20 μ s after photolysis, because they were derived from at least two-photon process. The rest of C_7H_7 solely from 1PD was tested for their chemical reactivities toward toluene-*d*₈. In 640-nm photolysis, the laser power was adjusted to increase the 2PD signal of $C_7H_7^+$ while suppressing the 3PD signal of $C_5H_5^+$ below the detection limit, and all $C_7H_7^+$ products were analyzed. It has been well known that the benzyl cation undergoes reactions 1–3 with toluene-*d*₈, whereas the tropylium cation remains unreactive.^{14,19}

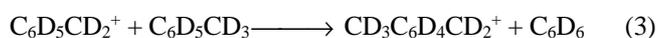
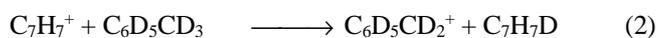
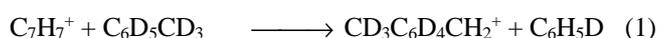


Table 2 summarizes the product branching ratio, [tropylium cation]/[benzyl cation], obtained from this work and the channel branching ratio, [channel I]/[channel II], for 1PD at

Table 2. The channel branching ratios, [channel I]/[channel II], and the product branching ratios, [tropylium⁺]/[benzyl⁺], of iodotoluene radical cations

	1PD at 532 nm		2PD at 640 nm	
	[ch I]/[ch II] ^a	[tr ⁺]/[bz ⁺]	[ch I]/[ch II] ^a	[tr ⁺]/[bz ⁺]
<i>o</i> -iodotoluene	55/45	4/96	98/2	8/92
<i>m</i> -iodotoluene	0/100	0/100	94/6	13/87
<i>p</i> -iodotoluene	0/100	0/100	77/23	4/96

^aReference 16.

532 nm and 2PD at 640 nm estimated from the RRKM rate-energy curves.^{3,16} When channel II was selected by photolyzing *m*- and *p*-isomers at 532 nm, all C₇H₇⁺ products reacted away, indicating the benzyl cation structure. When channel I was selected by photolyzing the *o*-isomer with two photon at 640 nm, a few percent of C₇H₇⁺ remained unreactive, indicating the presence of the tropylium cation. These tropylium cations must be derived from the isomerization of tolyl cations produced from channel I. The product branching ratios obtained in this work are in qualitative agreement with those reported by Jackson *et al.*⁶ using EI in an ICR cell. Because the channel branching ratio is available as a function of internal energy, the isomerization branching ratio of the *o*-, *m*-, *p*-tolyl cations are derived. They are 0.089, 0.16, and 0.055 for *o*-, *m*-, and *p*-tolyl cations, respectively. Results are given in Table 3.

The present result with iodotoluene radical cations provides direct evidence that channel I leads to the tolyl cations that isomerize to both tropylium and benzyl cations, and confirms our previous conclusion with bromotoluene radical cations that channel II leads predominantly to the benzyl cation. However, the mechanism of isomerization is still elusive. Recent theoretical work at a B3LYP/6-31G(d,p) level²⁰ presented activation barriers of 1.08 eV for the H-atom migration from the *o*-tolyl cation to benzyl, 1.17 eV for the rearrangement of the *o*-tolyl cation to tropylium *via* benzyl, 1.96 eV for the isomerization of the *m*-tolyl cation to *ortho*, and 2.05 eV for the H-atom migration in the phenyl cation. The H-atom migration from the *p*-tolyl cation to *meta* is expected to have an activation barrier similar to that in the phenyl cation. Thus, if the H-atom migration is the mechanism of isomerization of the tolyl cations to benzyl or tropylium, theoretical activation barriers to the benzyl cation are 1.08, 1.96, and 2.05 eV for *o*-, *m*-, and *p*-tolyl cations, respectively, and those to the tropylium cation are 1.17, 1.96, and 2.05 eV, respectively. In experiment, the 2PD at 640 nm

Table 3. The isomerization branching ratios of the tolyl cations from channel I

	[tropylium ⁺]/[benzyl ⁺] ^a	
	1PD at 532 nm	2PD at 640 nm
<i>o</i> -tolyl	0.078	0.089
<i>m</i> -tolyl	—	0.16
<i>p</i> -tolyl	—	0.055

^a[tropylium⁺]/[benzyl⁺] = [tr⁺]/[ch I].

releases 1.76, 1.63, and 1.46 eV excess energies in channel I for *o*-, *m*-, and *p*-iodotoluene radical cations, respectively. On the other hand, the 1PD at 532 nm provides 0.22 and 0.09 eV excess energies in channel I for *o*- and *m*-iodotoluene radical cations, respectively. For *para*, the channel I threshold is greater than the one-photon energy at 532 nm. When compared with theory, if the H-atom migration is the only mechanism of isomerization of the tolyl cations, we should not have detected the tropylium cation from both 1PD of the *o*-isomer at 532 nm and 2PD of *m*- and *p*-isomers at 640 nm. Moreover, the formation of the tolyl cation itself from channel I has been firmly established as evidenced by the ion-molecule reaction with dimethyl ether.²¹ Thus, to account for our results as well as others, the more elaborate mechanism than the H-atom migration needs to be considered. Further theoretical investigations are called for.

Conclusion

In unimolecular dissociations of iodotoluene radical cations, the lowest barrier rearrangement channel II leads exclusively to the formation of the benzyl cation, whereas the direct C-I cleavage channel I yields the tolyl cations that isomerize to both benzyl and tropylium cations with dissimilar branching ratios among *o*-, *m*-, and *p*-isomers. The isomerization of tolyl cations involves more than H-atom migration in the mechanism.

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