

Time- and product-resolved photodissociations of bromotoluene radical cations

Byungjoo Kim and Seung Koo Shin

Citation: The Journal of Chemical Physics **106**, 1411 (1997); doi: 10.1063/1.473289 View online: http://dx.doi.org/10.1063/1.473289 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/106/4?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Gas-phase electronic spectroscopy of the indene cation (C9H8 +) J. Chem. Phys. **138**, 224307 (2013); 10.1063/1.4808380

Photodissociation of gaseous CH3COSH at 248 nm by time-resolved Fourier-transform infrared emission spectroscopy: Observation of three dissociation channels J. Chem. Phys. **138**, 014302 (2013); 10.1063/1.4768872

Product branching ratios in photodissociation of phenyl radical: A theoretical ab initio/Rice–Ramsperger–Kassel–Marcus study J. Chem. Phys. **136**, 234305 (2012); 10.1063/1.4726455

Two-dimensional cross-spectral correlation analysis and its application to time-resolved Fourier transform emission spectra of transient radicals J. Chem. Phys. **123**, 184104 (2005); 10.1063/1.2074147

Resolved high Rydberg spectroscopy of benzenerare gas van der Waals clusters: Enhancement of spin–orbit coupling in the radical cation by an external heavy atom J. Chem. Phys. **110**, 5589 (1999); 10.1063/1.478457



Time- and product-resolved photodissociations of bromotoluene radical cations

Byungjoo Kim and Seung Koo Shin

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

(Received 29 August 1996; accepted 14 October 1996)

Photodissociations of o-, m-, and p-bromotoluene radical cations have been studied in the wavelength range 575–475 nm using Fourier transform-ion cyclotron resonance (FT-ICR) mass spectrometry. The parent ions were prepared by charge-transfer reactions of bromotoluenes with toluene- d_8 radical cations produced by two-photon ionization of toluene- d_8 at 266 nm. Bromotoluene radical cations dissociate to $C_7H_7^+$ by loss of Br. The dissociation rates were measured by time-resolved photodissociation spectroscopy. Structures of $C_7H_7^+$ from one-photon dissociation were identified by their bimolecular reactivities with toluene- d_8 . The C₇H₇⁺ products from all three isomers were identified as the benzyl cation. No unreactive tropylium ions were detected within experimental limits. The rate constants measured in this work were combined with the previous photoelectron-photoion-coincidence results to refine activation parameters for the Rice-Ramsperger-Kassel-Marcus rate-energy curves, k(E), for the low barrier rearrangement process. The activation barriers are estimated to be 1.66, 1.80, and 1.78 eV for the o-, m-, and *p*-bromotoluene radical cations, respectively, whereas the entropy changes for the activation, $\Delta S^{\ddagger}(1000 \text{ K})$, are -9.6, -7.2, and -5.6 eu., respectively. The mechanism of the rearrangement process is presented to account for the predominant formation of the benzyl cation. © 1997 American Institute of Physics. [S0021-9606(97)00604-1]

I. INTRODUCTION

Unimolecular dissociations of halotoluene radical cations have attracted much interest in recent years for the elucidation of the mechanisms of the $C_7H_7^+$ formation.^{1–11} The halotoluene radical cations (Cl, Br, and I) with a few eV internal energy dissociate to $C_7H_7^+$ by loss of halogen. Olesik et al. measured rates of energy-selective dissociations of halotoluene radical cations (Cl, Br, and I) in the internal energy range 2.7-3.5 eV by using the photoelectron-photoion coincidence (PEPICO) technique.¹ Dunbar and co-workers measured rates of one-photon dissociation (1PD) of iodotoluene radical cations in the internal energy range 2.1-2.7 eV by time-resolved photodissociation (TRPD) spectroscopy.^{2,3} The structures of $C_7H_7^+$ products were studied in the separate experiments employing collisional activation (CA) mass spectrometry^{1,4-6} or ion cyclotron resonance (ICR) spectrometry.⁷ These studies provided a two-channel picture as shown in Fig. 1, following Dunbar's notation.³ The direct C-X (X=halogen) bond cleavage, denoted channel I, yields tolyl cations, whereas the rearrangement process, denoted channel II, produces either the benzyl or tropylium cation or both. The identity of $C_7H_7^+$ from channel II has not been well established, however, most workers have concluded that both isomers are formed with a preference to the tropylium ion.^{1-3,8} In structural studies,⁴⁻⁷ the $C_7H_7^+$ ions were produced mostly by electron impact (EI) that imparts a broad internal energy distribution to the parent ion.¹² Consequently, a number of structures identified from there do not correlate directly to the selected dissociation channels.

To help establish the mechanism of the $C_7H_7^+$ formation from channel II, the energy-selective studies of both the rates of dissociation and the structures of $C_7H_7^+$ products below

the dissociation threshold to channel I are needed. In this work, photodissociations of o-, m-, and p-bromotoluene radical cations were studied in the internal energy range 2.2-2.7 eV using Fourier transform ion cyclotron resonance (FT-ICR) spectrometry. Bromotoluene radical cations are chosen as they afford energy-selective access to channel II without opening channel I owing to a large gap in dissociation threshold between the two channels. For instance, thermochemical thresholds for channel I are 2.68, 2.58, and 2.90 eV for o-, m-, and p-isomers, respectively, 1,3,9,13 whereas activation barriers for channel II determined from PEPICO experiments in the internal energy range 2.7-3.5 eV are 1.80 eV for both o- and p-bromotoluene radical cations and 1.84 eV for the m isomer.¹ A number of structural studies were reported to date.^{1,4-7} Jackson et al. studied the structures of $C_7H_7^+$ from EI of bromotoluenes by observing their ionmolecule reactions with toluene using ICR spectrometry.⁷ They reported the branching ratio favoring the benzyl structure, [benzyl⁺]/[tropylium⁺], ranging from 99/1 at 14 eV to 93/7 at 25 eV, which was nearly identical among all three isomeric radical cations. In contrast to the ICR results, McLafferty and co-workers reported the opposite trend, [benzyl⁺]/[tropylium⁺]=18/82 at 70 eV, from the CA mass spectrometric studies.^{5,6} Olesik et al. reexamined the structures by CA methods and reported the branching ratio favoring the tropylium ion.¹

In order to overcome the deficiency of EI that lacks the energy selectivity, the parent ions were prepared by the photoionization-charge-transfer (PICT) method.¹² The PICT involves a sequence of ionization and charge-transfer processes 1–3.

$$C_6 D_5 C D_3 + 2h\nu(266 \text{ nm}) \rightarrow C_6 D_5 C D_3^{++} + e^{-},$$
 (1)

0021-9606/97/106(4)/1411/7/\$10.00



FIG. 1. A schematic illustration of the two-channel picture for dissociations of halotoluene radical cations.

$$C_6D_5CD_3^{+}+CH_3C_6H_4Br \rightarrow C_6D_5CD_3+CH_3C_6H_4Br^{+},$$
 (2)

$$CH_{3}C_{6}H_{4}Br^{+} + CH_{3}C_{6}H_{4}Br \rightarrow CH_{3}C_{6}H_{4}Br + CH_{3}C_{6}H_{4}Br^{+}.$$
(3)

The two-photon ionization of toluene- d_8 at 266 nm generated its radical cation. Because the ionization potential (IP) of toluene- d_8 , 8.83 eV,¹³ is higher than those of bromotoluenes, ~8.7 eV,¹ toluene- d_8 radical cations underwent the chargetransfer process 2 with bromotoluenes to yield bromotoluene radical cations. The vibrationally excited bromotoluene radical cations then relaxed by both radiative relaxation $^{14-16}$ and thermalization by self-charge-exchange reactions with the parent neutrals at room temperature.¹² Unlike EI, the PICT ensures a thermal internal energy distribution of the parent ion in the absence of resistive heating by hot filament.¹²

The parent ions were then optically excited to the excited electronic state by a second laser in the wavelength range 575-475 nm. The rapid internal conversion to the ground electronic state prepares vibrationally hot molecular ions.¹⁷ The wavelengths were chosen so as to excite the parent ions above activation barriers for channel II but below or near thermochemical thresholds for channel I. The rates of 1PD of bromotoluene radical cations were measured by TRPD spectroscopy.^{2,3,12,18} The rate constants measured in the internal energy range 2.2-2.7 eV were combined with the previous PEPICO data¹ in the internal energy range 2.7– 3.5 eV for the refinement of RRKM parameters. Structures of $C_7H_7^+$ products were identified at each wavelength by observing their ion-molecule reactions with toluene- d_8 . The identity of the $C_7H_7^+$ product combined with the activation parameters are used to establish the mechanism of the rearrangement process.

II. EXPERIMENT

Experimental setups were previously described in detail.¹² The FT-ICR spectrometer used in this work consists of a 5.0 T superconducting magnet (Oxford Magnet Inc.), a home-built vacuum chamber with a 2-in. cubic trapping ICR cell, and an IonSpec Omega/486 FT-data system. There were 0.325-in. holes in the centers of both trapping plates to provide optical access along the axial direction. The background pressure in the ICR chamber was typically below 9.0×10^{-10} Torr.

All chemicals were purchased from Aldrich Inc. and used without further purification except several freeze-pumpthaw cycles. Gaseous bromotoluene and toluene- d_8 were separately guided into the ICR cell by two electropolished stainless steel tubes connected to either a leak valve or a home-built pulsed valve. The purity of each sample was tested by taking EI mass spectra. Sample inlet lines were baked out and pumped out overnight to prevent any cross contaminations between isomers. EI mass spectra of residual background in the ICR chamber and the inlet lines were checked for contamination before introducing a new sample. The sample pressures were measured by observing the kinetics of ion-molecule reactions with known rate constants.^{12,19} Partial pressures of bromotoluenes and toluene- d_8 were kept constant at 4×10^{-8} and 2×10^{-8} Torr, respectively.

Two-photon ionization of toluene- d_8 was achieved by the 266 nm laser pulse from the frequency quadrupled output of a Nd:YAG laser (Spectra-Physics, GCR-150). A typical pulse width was ~ 10 ns. The unfocused UV laser beam of a 3 mm diameter was passed through the center of the ICR cell along the magnetic field axis. A typical laser power measured before entering a vacuum window was ~ 2 mJ/pulse. Photodissociation of bromotoluene radical cations was accomplished in the wavelength range 575-475 nm by a counterpropagating second laser beam that overlapped with the UV laser beam. A 532 nm laser pulse was the frequency doubled output of a Nd:YAG laser (Continuum, NY-8010). The longer wavelength range 555-575 nm was covered by a dye laser (Continuum, ND-6000) with Rhodamine-590 pumped by the 532 nm output of the Continuum Nd:YAG laser. The shorter wavelength range 495-475 nm was provided by the same dye laser with Coumarine-480 pumped by the 355 nm output of the Continuum Nd:YAG laser. The photodissociation laser beam was adjusted to a 2-mm diameter at a typical laser power of 1-3 mJ/pulse.

The photodissociation laser was delayed 2 s after twophoton ionization of toluene- d_8 . It ensures the completion of charge-transfer reactions of toluene- d_8 radical cations with bromotoluenes and the subsequent thermalization by selfcharge-exchange reactions with bromotoluene neutrals.¹² Because there is no resistive heating of the ICR cell by hot filament, the temperature of molecule is considered the same as the vacuum housing temperature (20 °C).¹²

For time-resolved detection of photodissociation processes, the temporal buildup of $C_7H_7^+$ was monitored as a function of time delay between the photodissociation laser and the beginning of radio-frequency (rf) detection pulse. The detection rf is in resonance with the ICR frequency of $C_7H_7^+$. The duration of the rf burst was set to 20 μ s for the slow kinetics measurements in the wavelength range 575-532 nm. As the dissociation rate increases in shorter wavelengths, the rf duration was reduced to 10 μ s. A precise timing of the photodissociation laser pulse was monitored by using a fast photodiode.

The bimolecular reactivities of $C_7H_7^+$ products toward toluene- d_8 were monitored at each wavelength by taking mass spectra at 20 s after photodissociation. The completion of ion-molecule reactions was checked by observing tempo-



FIG. 2. TRPD spectra of the *o*-bromotoluene radical cation at 570, 555, 532, and 495 nm. The solid curves are the calculated TRPD spectra using the convoluted signal Eq. (5) with the RRKM parameters reported in Table III.

ral variations of ion intensities. The benzyl cation reacts with toluene- d_8 to yield $\text{CD}_3\text{C}_6\text{D}_4\text{CH}_2^+$, while the tropylium cation remains unreactive.^{7,19–21}

III. TIME-RESOLVED DATA ANALYSIS

The ICR signal equation for the product ion is given in Eq. (4) for the photodissociation of the parent ion with a given internal energy E:^{12,18}

$$S[k(E),t] = C\Delta \left(1 - \exp[-k(E)t] \frac{1 - \exp[-k(E)\Delta]}{k(E)\Delta}\right),$$
(4)

where S[k(E),t] is the product ion intensity, *C* is the proportionality constant, Δ is the duration of the detection rf burst, k(E) is the dissociation rate constant for a given internal energy *E*, and *t* is the time delay between the photodissociation laser pulse and the beginning of the detection rf burst. As the dephasing rates for the parent and the daughter ions in a 5 T magnetic field are much faster than the dissociation rate, the parent ion correction term due to dephasing is not included in the signal Eq. (4). Because the parent ions produced by charge-transfer reactions were thermalized at the room temperature, the signal equation was convoluted with a thermal internal energy distribution of the parent ions:^{22,23}

$$\langle S(t) \rangle = \sum_{E_T=0}^{E_0} P(E_T) S[k(E), t],$$
 (5)

where $\langle S(t) \rangle$ is the convoluted signal equation and $P(E_T)$ is a truncated Boltzmann distribution of the parent ion with a dissociation threshold, E_0 . *E* is the sum of a thermal internal energy and a photon energy, $E = E_T + h\nu$.

A typical procedure for the rate-energy curve fitting is as follows.¹² First, the TRPD data were fitted to a single exponential curve to give an approximate rate constant at each wavelength. The approximate rate constants as a function of average internal energy, $E = \langle E_T \rangle + h\nu$, were then used to set



FIG. 3. TRPD spectra of the *m*-bromotoluene radical cation at 570, 555, 532, and 495 nm.

the initial rate-energy curve parameters for RRKM calculations. Second, the convoluted signal Eq. (5) was used to calculate the TRPD data at each wavelength to compare with the experiments. Last, the RRKM parameters were refined iteratively until the TRPD curves calculated using the Eq. (5) best fitted experiments at all wavelengths.

IV. RESULTS

A. Time-resolved photodissociation (TRPD) spectra and RRKM parameters

TRPD spectra of o-, m-, and p-bromotoluene radical cations are shown in Figs. 2, 3, and 4, respectively. TRPD spectra for all three isomers show nonzero product yields at t=0 owing to two-photon processes as reported previously.¹² The rate of two-photon dissociation is much faster than the time scale of the rf burst duration. The relative intensity of time-zero intercept increases as the laser power increases, confirming that the initial fast rising components during rf burst excitation result from at least two-photon process.



FIG. 4. TRPD spectra of the p-bromotoluene radical cation at 575, 555, 532, and 495 nm.

TABLE I. Average dissociation rate constants of bromotoluene radical cations.

Wavelength	$\langle FT \rangle + hy$	$k (s^{-1})^a$		
(nm)	eV	ortho	meta	para
575	2.258			2000 ± 100
570	2.277	6900 ± 600	1100 ± 100	
555	2.336	11900 ± 1000	1800 ± 200	4700 ± 400
532	2.430	23000 ± 1500	3700 ± 200	8700± 500
495	2.606	50000 ± 3600	20000 ± 700	31000 ± 1400
475	2.712		45000±5000	

^aErrors are estimated from the uncertainty of fitting TRPD spectra.

Hence, the photodissociation laser power was adjusted in such a way to make 1PD become dominant in the TRPD spectra.

The solid lines drawn in Figs. 2–4 along with experimental data are the best-fit curves using the convoluted signal Eq. (5) based on the refined RRKM parameters. The calculated curves fit the experimental data very well at all wavelengths. The average dissociation rate constant obtained at each wavelength is summarized in Table I. In the common internal energy range 2.34-2.61 eV, the average rate constants are $11.9-50 \times 10^3 \text{ s}^{-1}$ for *o* isomer, $1.8-20 \times 10^3 \text{ s}^{-1}$ for *m* isomer, and $4.7-31 \times 10^3$ s⁻¹ for the *p* isomer. Since the rates of 1PD are much faster than the infrared-radiative relaxation rate of 160 s⁻¹ reported for the *p*-iodotoluene ion,² the radiative relaxation processes are not included in data analyses. The dissociation rate decreases in order; ortho, para-, and meta-isomers. The same trend was previously observed from 1 PD of iodotoluene radical cations at 532 nm in our laboratory.24

The average rate constants are plotted as a function of average internal energy in Figs. 5, 6, and 7 for o, m, and p species, respectively. The solid symbols represent this work and the open symbols denote the PEPICO results from the Ref. 1. For comparisons, the rate-energy curves for the direct



FIG. 6. RRKM rate-energy curves for the *m*-bromotoluene radical cation.

C-Br dissociation channel I are also included in Figs. 5-7 as dotted lines. They are calculated by using thermochemical thresholds summarized in Table II. The entropy changes for channel I are assumed to be the same for all three isomers as those of iodotoluene radical cations, $\Delta S^{\ddagger}(1000 \text{ K}) = 7.6 \text{ eu.}^{3,8}$ In the present wavelength range, average internal energies of o and p isomers are less than thermochemical thresholds for channel I, whereas those of the m isomer in the 495–475 nm range lie above the threshold for channel I. Since the dissociation rate to channel I is several orders of magnitude slower than that to channel II, the relative yield of channel I must be less than 0.1% even with the highest energy studied in the PEPICO experiments. Hence, the previous PEPICO data in the internal energy range 2.7-3.5 eV are combined with the present results in the internal energy range 2.2-2.7eV to derive the RRKM parameters for channel II. Table III lists the RRKM parameters that fit both experiments. The activation barriers, E_0 , are 1.66, 1.80, and 1.78 eV for o-, m-, and p-bromotoluene radical cations, respectively. The entropy changes for activation, $\Delta S^{\ddagger}(1000 \text{ K})$, are -9.0 eu for ortho, -7.2 eu for meta, and -5.6 eu for para isomers, which indicates the tight transition states for channel II.



FIG. 5. RRKM rate-energy curve for the *o*-bromotoluene radical cation. Solid symbols denote the data from this work and open symbols from the previous PEPICO studies. The solid line represents the RRKM rate-energy curve for channel II and the dotted line is for channel I.



FIG. 7. RRKM rate energy curves for the *p*-bromotoluene radical cation.

TABLE II. Thermochemical data for chemical species related to this work.

М	$IP(M) \ (eV)^a$	$\Delta H^0_{f,0}(M^+) \ (\text{kJ mol}^{-1})^{\text{a}}$
o-CH ₃ C ₆ H ₄ Br	8.64 ± 0.01	937
m-CH ₃ C ₆ H ₄ Br	8.73 ± 0.01	943
<i>p</i> -CH ₃ C ₆ H ₄ Br	8.67 ± 0.01	932
$C_6D_5CD_3$	8.83 ^{b,c}	924 ^c
$C_6H_5CH_2$ (benzyl)	7.20 ^c	919
c-C ₇ H ₇ (tropylium)	6.24 ^c	8.71 ^{a,b}
$o-C_6H_4CH_3$ (o-tolyl)		$(1078)^{d}$
$m - C_6 H_4 C H_3 (m - tolyl)$		1074
$p-C_6H_4CH_3$ (<i>p</i> -tolyl)		1094
$\Delta H_{f,0}(\text{Br})^{a} = 117.9 \text{ kJ mol}^{-1}$		

^aReferences 1, 25, 26.

^bReference 27.

^cReference 13.

^dEstimated from the activation barrier, 2.11 eV, for the direct dissociation of *o*-iodotoluene radical cation (Ref. 3).

Figure 8 combines the rate-energy curves for all three isomeric ions for direct comparisons. The metabromotoluene radical cation shows the slowest dissociation in the entire energy range. The *o* isomer dissociates faster than the para isomer in the low energy regime, while the PEPICO results show comparable dissociation rates for both isomers in the high energy regime starting from ~ 2.7 eV. The slope of the rate-energy curve that indicates the tightness of the transition state becomes less negative in going from *ortho* to *meta* to *para* isomers. In the case of *ortho* isomer, the PEPICO data deviates significantly from the RRKM fit in the intermediate energy regime.

B. The structures of C₇H₇⁺ products

Because the products ions formed within the first 20 μ s were originated from more than one-photon processes, they were ejected out of the ICR cell by applying an ejection rf pulse after 20 μ s from photodissociation. The rest of C₇H₇⁺ ions, resulted solely from 1PD, were analyzed for their reac-



FIG. 8. RRKM rate-energy curves for channel II of all three isomers. The solid symbols are the experimental data from this work and the open symbols from the previous PEPICO studies.

TABLE III. RRKM kinetic parameters E_0 (eV) and $\Delta S^{\ddagger}(1000 \text{ K})$ (eu) for the bromotoluene radical cations.^a

	ortho	meta	para
(a) Channel I ^a			
E_0^{a}	1.66	1.80	1.78
ΔS^{\ddagger}	-9.0	-7.2	-5.6
(b) Channel II ^b			
E_0	2.68	2.58	2.90
ΔS^{\ddagger}	7.6	7.6	7.6

^aThe estimated errors are ± 0.02 eV.

 ${}^{b}E_{0}$'s are estimated from thermochemical thresholds for the direct dissociation and ΔS^{\ddagger} 's are from the iodotoluene ion system (Refs. 3 and 8).

tivities with toluene- d_8 . All $C_7H_7^+$ ions underwent reaction 8 to completion and yielded $CD_3C_6D_4CH_2^+$, indicating the benzvl structure.^{7,19–21,28}

$$C_7H_7^+ + C_6D_5CD_3 \rightarrow CD_3C_6D_4CH_2^+ + C_6H_5D.$$
 (8)

No unreactive components were observed even after 20 s, suggesting the absence of the tropylium ion from 1PD in the present wavelength range. It is concluded that the rearrangement channel II leads to the formation of the benzyl ion in all three isomeric ions.

Meanwhile, when all $C_7H_7^+$ products from both one- and two-photon processes were analyzed, there remained a small fraction of $C_7H_7^+$ unreactive. They are most likely from a two-photon process. The previous studies in our laboratory revealed that the tolyl cations from 2PD of iodotouene radical cations at 640 nm isomerize mostly to the benzyl ion with a small fraction of the tropylium ion.²⁴ It is suggested that the unreactive tropylium ions result from the isomerization of tolyl cations from two-photon process. Further quantitative analyses for the two-photon products were not performed.

V. DISCUSSIONS

One of the most important results from this study is the identification of the structures of $C_7H_7^+$ products from channel II in conjunction with the rates of energy-selective dissociations of bromotoluene radical cations. It was previously suggested from the CA mass spectrometric studies that the rearrangement channel II led to both the benzyl and tropylium cations.^{1,2,5} To the contrary, herein, we provide evidence against the formation of the tropylium ion in channel II from all three isomeric ions. Similar results were previously observed from iodotoluene radical cations.²⁴ The chlorotoluene radical cations are expected to yield similar results to those of both bromo- and iodotoluene radical cations. The discrepancy between the present study and the earlier CA studies may be due to the difference in preparation of $C_7H_7^+$. In CA studies, the ionizing electron energy was 70 eV and the source temperature was 150 °C, whereas, in the present study, the bromotoluene radical cations were prepared at room temperature by the PICT and $C_7H_7^+$ was produced by energy-selective photodissociations. The observation of the tolyl structure in CA studies indicates that the internal energy of the precursor ion from EI may have been significantly



FIG. 9. The proposed mechanism of dissociations of bromotoluene radical cations to $C_7H_7^+$ with a loss of Br.

higher than the channel I threshold. The EI also permits different isomers of bromotoluene to be formed, thereby leading to different product ion structures. The present results certainly raise questions about the validity of many EI/CA results on the structure of the lowest barrier product.

It is interesting to see that activation parameters do not differ significantly among o, m, and p isomers. In addition, the activation parameters are not affected very much by the halogen substitution (Cl, Br, and I). For chlorotoluene radical cations, Olesik et al. reported activation barriers of 1.70 eV for the ortho isomer and 1.77 eV for both meta- and para isomers.¹ For iodotoluene radical cations, Dunbar and coworker determined activation barriers of ~ 1.88 eV for all three isomers.^{2,3} These similarities in the product structures and kinetics among different halotoluenes provide a newer insight into the intramolecular rearrangement process in halotoluene radical cations. First, the halogen atom is not considered to be an active species that migrates in the rearrangement process. Second, the C-X (X=halogen) bond cleavage occurs at the final step after forming precursors for the benzyl cation. Last, the halogen atom may affect the rearrangement process by forming resonance structures. McLafferty and Bockhoff have previously proposed the isomerization of halotoluene radical cations to methylene-cyclohexadienyl halide radical cations to account for the benzyl ion formation.⁴ Our observations lend experimental supports to the McLafferty rearrangement, although the existence of such reaction intermediates needs to be verified by experiments.

Figure 9 illustrates the mechanism modified from that of McLafferty et al.⁴ to account for the present results in conjunction with other relevant experimental¹⁻¹¹ and theoretical studies.^{27,29–33} The first step is the [1,2] or [1,3] sigmatropic migration of an α -H atom to the ipso- or ortho-position, respectively. The second and subsequent steps include the [1,2] or [1,4] CH₂ migration and [1,2] H-atom migration. No theoretical transition state calculations are available for halotoluene radical cations. In the case of toluene radical cation, *ab initio* calculations predict a lower barrier for [1,2] α -H migration than [1,3] α -H migration.²⁹ With halotoluenes, however, the positive charge may be localized near halogens by forming partial double-bond resonance structures that perturb electronic configurations of the ring carbons. Thus, the barrier height as well as the direction of H-atom migration can be significantly modified from the toluene system. The positive charge character delocalized on the halogen atom is evident in photoelectron spectra of halobenzenes and halotoluenes.34-36

A. The [1,2] α -H migration

The [1,2] α -H migration is a well-known rearrangement process in carbonium ions.^{30,33} Once formed, intermediate radical cations can subsequently undergo either [1,2] or [1,4]CH₂ migrations and/or [1,2] H migrations. The benzyl ion precursors can be formed by the [1,2] H migration in the ortho-isomer, or by the sequential [1,4] CH₂ and [1,2] H migrations in the meta-isomer, or by the [1,4] CH₂ migration in the para-isomer. The [1,2] CH₂ migration may lead to an insertion of CH₂ into a C-C bond to form the cycloheptatrienyl halide radical cation as a precursor for the tropylium ion. The [1,4] CH₂ migration may involve bicyclo-[2,2,1]-hepta-2,5-dienyl halide radical cations as local minima along the reaction coordinate. The energetics of both [1,2] and [1,4] CH₂ migrations are not well established. The barrier for the [1,2] H migration along the benzene ring is estimated to be $\sim 0.8 \text{ eV}.^{31}$

B. The [1,3] α -H migration

The [1,3] α -H migration is not a favored process in neutral systems.³⁰ For the radical cations, however, it may be comparable in energetics to the [1,2] α -H migration.³³ The [1,3] α -H migration forms the methylene-cyclohexadienyl halide radical cations in o-isomer by one step. For meta- and para-isomers, the formation of benzyl ion precursors involves the subsequent [1,2] H migrations. The difference between [1,2] and [1,3] α -H migrations is in the CH₂ migration. The former process involves both CH₂- and H-atom migrations, whereas the latter process relies only on the H-atom migration. Therefore, the [1,3] α -H migration can lead to the exclusive formation of the benzyl ion without branching to the tropylium ion.

Though there is no direct evidence for or against the [1,2] α -H migration mechanism, the absence of tropylium ion favors the [1,3] α -H migration as the primary step in the rearrangement processes. This model predicts a lower activation barrier for the o-bromotoluene radical cation than mand *p*-isomers, as the bromine in the ortho position helps develop a more positive charge character on the ortho carbon. It is well known that the positive charge character helps the H atom to migrate in radical cations.³⁰ In cases of chlorotoluene radical cations, the ortho-isomer has a lower barrier than other isomers.¹ For iodotoluene radical cations, the rates of 1PD at 532 nm decreases in order of ortho-, para, and meta-isomers, similar to those observed in bromotoluene radical cations.²⁴ On the other hand, if the [1,2] α -H migration is the primary step, the subsequent H- or CH₂-migration

VI. CONCLUSION

The rates of energy-selective dissociations of bromotoluene radical cations as well as the structures of the corresponding $C_7H_7^+$ products were determined using FT-ICR spectrometry. In contrast to the widely accepted presumption that the lowest activation barrier rearrangement process leads to both the benzyl and tropylium ions with a preference to the tropylium ion, the present study reveals the benzyl cation as the predominant rearrangement product. The primary source of the tropylium ion in unimolecular dissociations of halotoluene radical cations is considered to be the isomerization of tolyl cations produced via the direct C-X bond cleavage. The rate measurement below thresholds of the direct C-Br bond cleavage allows the accurate determination of activation parameters for the rearrangement process. The proposed mechanism calls for theoretical investigations.

ACKNOWLEDGMENTS

S.K.S. acknowledges the support from the National Science Foundation Grant No. CHE-9302959, the National Science Foundation Young Investigator Award CHE-9457668. This work was also made possible by the Santa Barbara Laser Pool under NSF Grant No. CHE-9413030.

- ¹S. Olesik, T. Baer, J. C. Morrow, J. J. Ridal, J. Buschek, and J. L. Holmes, Org. Mass Spectrom. 24, 1008 (1989).
- ²R. C. Dunbar and C. Lifshitz, J. Chem. Phys. 94, 3542 (1991).
- ³C. Y. Lin and R. C. Dunbar, J. Phys. Chem. 98, 1369 (1994).
- ⁴F. W. McLafferty and F. M. Bockhoff, Org. Mass Spectrom. 14, 183 (1979)
- ⁵F. W. McLafferty and J. Winkler, J. Am. Chem. Soc. 96, 5182 (1974).
- ⁶C. J. Proctor and F. W. McLafferty, Org. Mass Spectrom. 18, 193 (1983).

- ⁷J.-A. A. Jackson, S. G. Lias, and P. Ausloos, J. Am. Chem. Soc. 99, 7515 (1977).
- ⁸Y. S. Cho, M. S. Kim, and J. C. Choe, Int. J. Mass. Spectrom. Ion Processes 145, 187 (1995).
- ⁹R. C. Dunbar, J. P. Honovich, and B. Asamoto, J. Phys. Chem. 92, 6935 (1988).
- ¹⁰R. C. Dunbar and G. H. Weddle, J. Phys. Chem. **92**, 5706 (1988).
- ¹¹C. Lifshitz, I. Levin, S. Kababia, and R. C. Dunbar, J. Phys. Chem. 95, 1667 (1991).
- ¹²S. K. Shin, S. J. Han, and B. Kim, Int. J. Mass. Spectrom. Ion Processes (in press).
- ¹³S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, J. Phys. Chem. Ref. Data 17, Suppl. 1 (1988).
- ¹⁴R. C. Dunbar, J. Phys. Chem. **91**, 2801 (1987).
- ¹⁵R. C. Dunbar, J. Chem. Phys. **90**, 7369 (1989).
- ¹⁶R. C. Dunbar, Mass Spectrom. Rev. 11, 309 (1992).
- ¹⁷R. C. Dunbar, in Gas Phase Ion Chemistry, edited by M. T. Bowers (Academic, New York, 1979), Vol. 3, Chap. 20.
- ¹⁸R. C. Dunbar, J. Phys. Chem. **91**, 2801 (1987).
- ¹⁹P. Ausloos, J.-A. A. Jackson, and S. G. Lias, Int. J. Mass. Spectrom. Ion Processes 33, 269 (1980).
- ²⁰S. Wexler and R. P. Clow, J. Am. Chem. Soc. **90**, 3940 (1968).
- ²¹P. Ausloos, J. Am. Chem. Soc. 104, 5259 (1982).
- ²²F. S. Huang and R. C. Dunbar, Int. J. Mass. Spectrom. Ion Processes 109, 151 (1991).
- ²³J. D. Faulk, R. C. Dunbar, and C. Lifshitz, J. Am. Chem. Soc. 112, 7893 (1990).
- ²⁴S. K. Shin, B. Kim, R. L. Jarek, and S.-J. Han (unpublished).
- ²⁵T. Baer, J. C. Morrow, J. D. Shao, and S. Olesik, J. Am. Chem. Soc. 110, 5633 (1988).
- ²⁶J. C. Treager and R. G. McLoughlin, Int. J. Mass Spectrom. Ion Phys. 27, 319 (1978).
- ²⁷C. Lifshitz, Acc. Chem. Res. 27, 138 (1994).
- ²⁸J. Shen, R. C. Dunbar, and G. A. Olah, J. Am. Chem. Soc. **96**, 6227 (1974).
- ²⁹C. Lifshitz, Y. Gotkis, A. Ioffe, J. Laskin, and S. Shaik, Int. J. Mass. Spectrom. Ion Processes 125, R7 (1993).
- ³⁰R. A. Woodward and R. Hoffman, The Conservation of Orbital Symmetry (Academic, New York, 1971).
- ³¹W. J. van der Hart, J. Am. Soc. Mass Spectrom. 6, 513 (1995).
- ³²C. Cone, M. J. S. Dewar, and D. Landman, J. Am. Chem. Soc. 99, 372 (1977).
- ³³M. J. S. Dewar and D. Landman, J. Am. Chem. Soc. **99**, 2446 (1977).
- ³⁴K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules (Halsted, New York, 1981).
- ³⁵D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, Molecular Photoelectron Spectroscopy (Wiley-Interscience, London, 1970).
- ³⁶E. W. Fu, P. P. Dymerski, and R. C. Dunbar, J. Am. Chem. Soc. 98, 337 (1976).