

Hyperthermal Collision-induced Dissociation of Bromotoluene Radical Cations at Self-Assembled Monolayer Surfaces

Sung-Chan Jo^{a,*}, Rodinei Augusti^b, and R. Graham Cooks^{c,*}

^aLCD R&D Center, LCD Division, Samsung Electronics, Co., Ltd. Yongin-Si, Kyeonggi-Do, 446-711 Korea

^bDepartment of Chemistry, Federal University of Minas Gerais, Belo Horizonte/MG Brazil

^cDepartment of Chemistry, Purdue University, West Lafayette, IN 47907, USA

Received March 7, 2011; Revised March 13, 2011; Accepted March 13, 2011

First published on the web March 15, 2011; DOI: 10.5478/MSL.2011.2.1.024

Abstract: Hyperthermal ion/surface collisions of bromotoluene radical cations were studied using perfluorinated (F-SAM) and hydroxyl-terminated (OH-SAM) self-assembled monolayer surfaces in a tandem mass spectrometer with BEEQ geometry. The isomers were differentiated by ion abundance ratios taken from surface-induced dissociation (SID). The dissociation rate followed the order of *ortho* > *meta* > *para* isomers. The peak abundance ratio of *m/z* 51 to *m/z* 65 showed the best result to discern the isomers. A dissociation channel leading to tolylium ion was suggested to be responsible for the pronounced isomeric differences. The capability of SID to provide high-energy activation with narrow internal energy distribution may have channeled the reaction into the specific dissociation pathway, also facilitating small differences in reaction rates to be effective in the spectral time window of this experiment. All of the molecular ions experiencing reactive collisions with the F-SAM surface undergo transhalogenation, in which a fluorine atom on the surface replaces the bromine in the incoming ions. This reactive collision was dependent on the laboratory collision energy occurring in *ca.* 40–75 eV range.

Key words: Ion/surface Collisions, Surface-induced Dissociation (SID), Bromotoluene, Isomer, Self-assembled Monolayer (SAM), Hyperthermal Energy

Introduction

Electron ionization (EI) is widely used for analysis owing to the rich fragmentations that reflect the detailed microchemical structures. However, differentiation of structural isomers with EI is often difficult, though there are some successful examples.¹ Such weakness especially in aromatic ring systems was well exemplified by the haloaromatic compounds with ethyl or smaller substituents.^{2,3}

To overcome the limitation, collision-induced dissociation (CID) was adopted for isomeric quantitation of the *m/z* 91 ions by analyzing peak abundances.⁴ However, the CID method required constant collisional cross-sections for all the isomers or it failed.⁵ Ion/molecule reaction was suggested as an alternative for the isomeric compositional analysis of C₇H₇⁺ ions⁶ and the physical chemistry was investigated on the two competing reactions leading to benzylium and tropylium ions.^{7,8}

Dunbar and the colleagues studied the dissociation kinetics of meta isomers of bromo- and iodotoluene ions using kinetic energy release (KER) as well as slow time-resolved photo-dissociation (TRPD) spectrometry and proposed two highly competing reactions through tight transition state along with the third one via simple cleavage.^{9–12} The rearrangement path-

way was believed to produce benzylium and tropylium ions with lower critical energy, whereas the other simple cleavage reaction results in tolylium ion at high internal energy. Figure 1 shows these channels with *p*-bromotoluene as an example.

On the other hand, the analyses of isomeric ion compositions left an interesting argument about the reaction products. A photoelectron-photoion coincidence (PEPICO) experiment on halotoluene molecular ions revealed that the rearrangement pathway favors the tropylium ion structure,¹³ but that was opposite to an ion cyclotron resonance mass spectrometer (ICR-MS) approach with EI. Shin and Kim reexamined the dissociation of bromotoluene molecular cations with photo-ionization-charge-transfer (PICT) method at room temperature

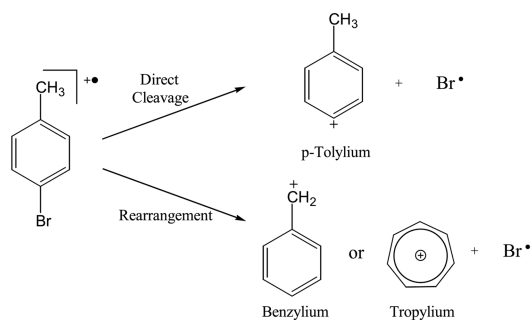


Figure 1. Schematic diagram and definition of the reaction channels in the dissociation of *p*-bromotoluene.

*Reprint requests to Dr. Sung-Chan Jo and Prof. R. Graham Cooks
E-mail: enigma.jo@samsung.com and cooks@purdue.edu

to reach the conclusion that tropylium was a result of the consecutive dissociation from tolylium ion because it was found in small amount only after two photon excitation whose energy barely overcame the activation barrier leading to the simple cleavage.^{7,8} Though there were slight disagreements in the actual number of the critical energies, it has been unanimously stated that the entropies of activation for the rearrangement are negative regardless of the isomers, whereas those for the simple cleavage are positive.

In tandem mass spectrometry, surface-induced dissociation (SID) emerged as an alternative to CID and was a great success in the analyses of isomeric ions.^{14–17} The major reason for such capability was rationalized an efficient activation with narrow internal energy distribution compared to CID. It was also demonstrated that SID show extensive fragmentation as well as reduced tendency to rearrangement leading to a common ion structure, which are advantageous for isomeric discrimination.

Isomeric structural analysis had been rare for halotoluenes, even if there were many research efforts on the kinetics and thermochemistry. Therefore, hyperthermal ion/surface collision study was performed for bromotoluene molecular ions in view of isomer discrimination with all these advantages of SID. The critical energies for the simple cleavage pathways have larger differences than the rearrangement channels, which encouraged this approach as shown in Table 1. The comparison of SID with CID was another point of discussion in this report.

Experimental

A custom-built hybrid tandem mass spectrometer with BEEQ configuration (B for magnetic sector, E for electric sector, and Q for quadrupole mass analyzer, respectively) was used for the SID study. Bromotoluenes were introduced into the EI source through a Granville-Phillips leak valve, ionized by 70 eV electron beam, and accelerated by a potential of approximately 1990 V in the source. The source temperature was approximately 18 °C and the pressure was maintained at 1.5×10^{-5} torr during experiment. The translational or collision energy of a projectile ion was defined by the difference in electrical potentials between the surface and the ion source. The incident angle of the ion beam was 55° relative to the surface normal, and the product ions were extracted at 90° to the incoming ion beam.

Table 1. Critical energies E_0 and entropy changes for activation ΔS^\ddagger (1000 K)(eu) for the dissociation of bromotoluene molecular cations obtained with PICT-ICR.⁸

	o-BrTol	m-BrTol	p-BrTol
Rearrangement			
E_0 (eV)	1.66	1.80	1.78
ΔS^\ddagger (eu)	-9.0	-7.2	-5.6
Direct cleavage			
E_0 (eV)	2.68	2.58	2.90
ΔS^\ddagger (eu)	7.6	7.6	7.6

A commercial triple stage quadrupole instrument manufactured by Finnigan (San Jose, CA) was used for CID experiments of bromotoluene isomers as well as gas phase ion/molecule reaction. The source temperature was 150 °C and the parent ion was generated by 70 eV electron beam. The collision cell pressure was indirectly measured by the manifold pressure when the ion/molecule reaction was being performed with perfluorohexane.

Hydrocarbon self-assembled monolayer (H-SAM), hydroxyl-terminated SAM (HO-SAM), and perfluorinated SAM (F-SAM) were prepared on cleaned pieces of-gold-coated silicon wafer by immersing the wafer pieces in ethanolic solutions of undecanethiol, 11-mercapto-1-undecanol (both ca. 1 mM), and 2-perfluorooctylethyl disulfide (~0.5 mM) for a week, respectively.

Three bromotoluene isomers and 11-mercapto-1-undecanol were purchased from Aldrich Inc. (Milwaukee, WI) and used as received. 2-perfluorooctylethyl disulfide was synthesized in this laboratory. The gold-coated silicon wafer was bought from International Wafer Service Inc. and comprised crystal orientation of (100) for the silicon layer.

Results and Discussion

Isomer discrimination

The SID spectra for the three isomers taken at 75 eV laboratory collision energy are shown in Figure 2. It shows the dissociation rate order of ortho>para>meta isomers in descending order, which is deduced from the ion abundances in the lower mass

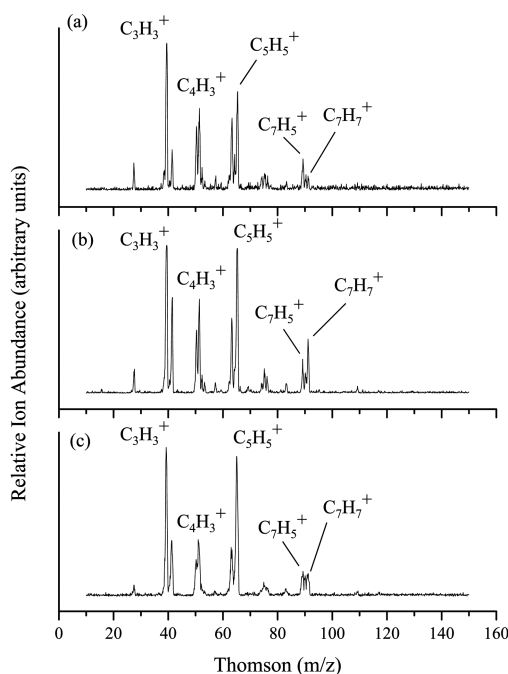


Figure 2. The SID mass spectra of (a) ortho, (b) meta, and (c) para bromotoluene molecular cations taken at 75 eV laboratory collision energy. It is notable that the fragment ions have undergone severe hydrogen loss, which generally requires high activation energy.

ranges. The different critical energies of each isomer for the rearrangement reactions support the trend, as shown in Table 1. Ion abundance ratios are used to discern the spectral differences based on the SID data and the examples are shown in Figure 3. The ratio that best serves the purpose was $(m/z\ 51)/(m/z\ 65)$. The difference in the spectral pattern is dramatic between the ortho isomer and the other two throughout the collision energy range utilized in this experiment, whereas the dissimilarity between *m*- and *p*-bromotoluene only becomes significant at high collision energies. Bearing with the gas phase ion/molecule reactions that rely on the reactivity of tolylium ions with ether and alcohols, HO-SAM surface was used for SID. However, such an effect was not observed and the data demonstrated an HO-SAM provides a lower translational to vibrational (TV) energy conversion than an F-SAM. Figure 3(c) illustrates the isomer differentiation using HO-SAM SID by the ion abundance ratio of $(m/z\ 51)/(m/z\ 91)$

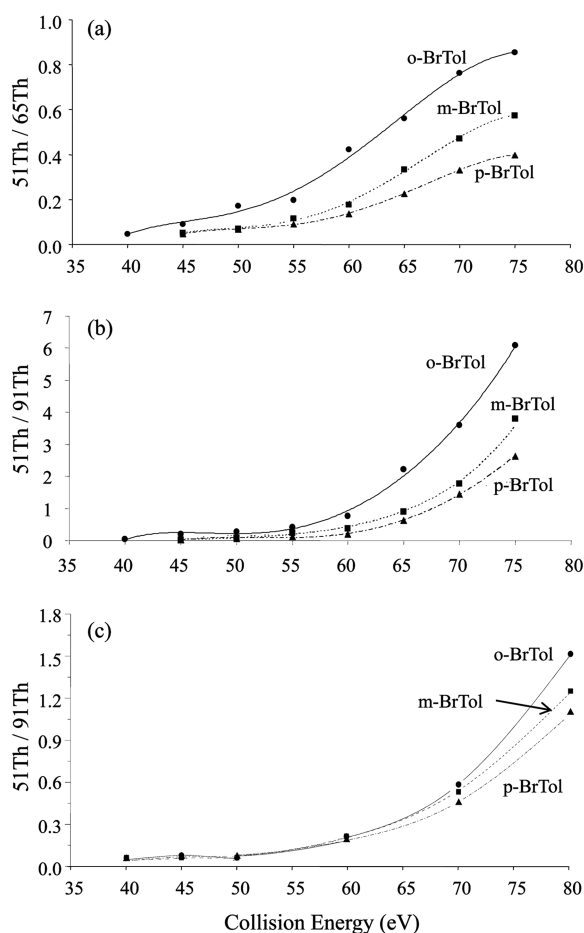


Figure 3. Peak abundance ratios for (a) $(m/z\ 51)/(m/z\ 65)$ and (b) $(m/z\ 51)/(m/z\ 91)$ pairs from the SID data taken at F-SAM surface. (c) The ratio, $(m/z\ 51)/(m/z\ 91)$ from the SID with HO-SAM surface. These abundance ratios show different trends in the high energy region suggesting different reaction kinetics. Each symbol denotes; -●- for ortho, -■- for meta, and -▲- for para isomers, respectively.

Though not shown in the current report, CID spectra of the isomeric ions taken at various collision energies under single collision condition showed no significant difference for the isomers, whereas slight differences were demonstrated under multiple collision condition.¹⁸ It is clear that the isomeric differentiation was more easily accomplished by SID compared to CID results and standard 70 eV EI mass spectra.

If the isomer discrimination should be effective, the dissociation channel should reflect the structural differences of their precursors leading to the thought that the pathway responsible for this capability is the direct cleavage. If it is correct, all or at least substantial contribution to the dissociation in the present study should occur through direct bond dissociation. Dunbar and coworker showed the overall rate-energy plot for iodotoluene isomers, where the same trend can be found as the present data. The dissociation rate of ortho isomer was considerably larger than the other two, while the pattern of the meta and para isomers look similar in the beginning. Considering that the simple cleavage prevails in iodotoluene dissociations, the SID behavior of bromotoluenes in this experiment seems to mainly rely on simple cleavage of C-Br bond. It is qualitatively supported by the fact that the discernment was better at higher collision energies. As was discussed earlier, the larger differences in activation energies for this direct cleavage further rationalizes this conclusion. The normal kinetic isotope effect observed in the dissociation of bromotoluene isomers by CID supports this conclusion, too.¹⁸

Transhalogenation reaction

A peak at $m/z\ 109$ was seen in the SID results regardless of the isomers, for which the examples are shown with the data taken at 55 eV of collision energy (Figure 4). The collision energy at which this process was observed was within 40 and 75 eV range. The same ion was not observed in corresponding experiments with a bare gold, hydrocarbon SAM, or hydroxyl-terminated SAM surfaces. Though ion/molecule reaction of bromotoluene isomers resulted in the same transhalogenation product with perfluorohexane as the reagent gas, it was not successful when Ar was used instead.¹⁸ However, the two isotopomers of bromotoluene ions, $m/z\ 170$ and 172 ions, produced the same result. Therefore, it was concluded that bromine atom is not incorporated in the structure of the ion at $m/z\ 109$. These results unanimously suggest that the ion at $m/z\ 109$ has the formula of $C_7H_7F^+$. The driving force for this interaction is rationalized by the stable C-F bond formation.

Transhalogenation reaction such as above has been observed during ion/surface collision when halogenated projectile ions were made to collide with an F-SAM and 4-membered ring activated complex was proposed as the reaction mechanisms.^{19,20} However, in this experiment, the reactivity of benzylium and tolylium ion structures reported previously was also suspicious as they may result in the same $m/z\ 109$ ion through F-abstraction from the surface followed by H radical loss. The open-shell $m/z\ 90$ ion had another possibility of taking a fluorine atom too, because such examples can be often found in ion/

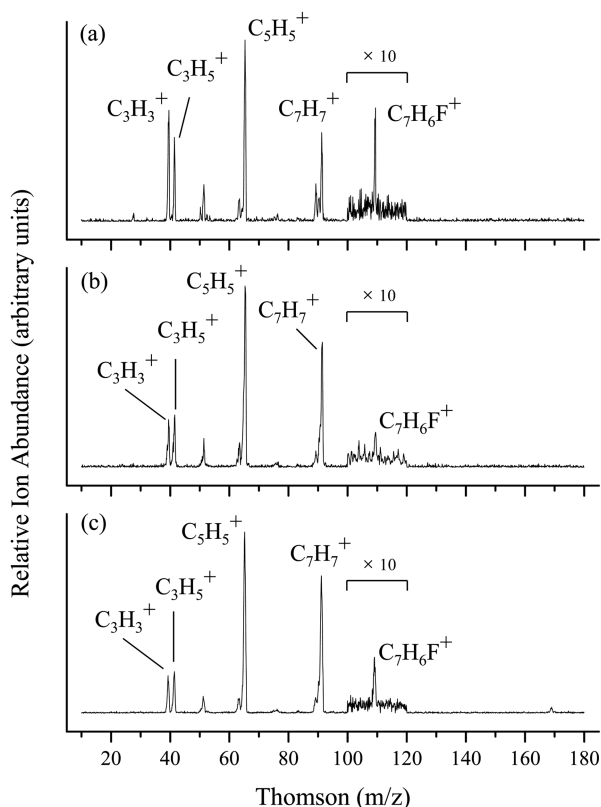


Figure 4. SID spectra of (a) ortho-, (b) meta-, and (c) para-bromotoluene cations taken at 55 eV of collision energy with F-SAM surface. The regions that include the ion at m/z 109 are magnified 10 times for better comparison.

surface collisions. The ions at m/z 90 and m/z 91 were chosen to investigate such possibilities to find no such reactivity leading to reconfirmation of the cyclic transition state proposed earlier. But it should be noted that the two ions chosen might not have the same structures as those produced during the ion/surface collisions.

Conclusions

Hyperthermal ion/surface collisions were applied to the isomer bromotoluene molecular ions using F-SAM and HO-SAM surfaces. The method was found effective to differentiate the bromotoluene isomers by the SID spectral patterns or a peak abundance ratio. The present method provided consistent spectral pattern unlike the standard 70 eV EI mass spectra and much better capability than CID spectra. The dissociation pathway that leads to tolylium ion was reasoned to be responsible for this discrimination, which needs the highest activation energy among all the reaction channels of bromotoluene isomers. In this regard, the property of SID that can highly activate ions with narrow distribution is deduced to make this isomeric discrimi-

mination possible. This speculation is supported by the less effective HO-SAM SID data as well as multiple collision CID spectra. The HO-SAM SID data confirmed lower TV conversion efficiency than F-SAM, as was clearly depicted by the peak abundance ratio (m/z 51)/(m/z 91).

During the ion/surface collisions, all the bromotoluene molecular cations underwent transhalogenation reaction exchanging their bromine with fluorine from the surface, supposedly via a concerted reaction with 4-membered ring transition state.

Even though the isomers are successfully analyzed, the detailed mechanism of this outcome is not thoroughly understood, calling for additional studies involving both theoretical and experimental approaches with isobaric ions from different parent ions. The major challenge regards to the rate-determining step, whether the direct cleavage or the ring expansion is the one. This method can be refined with better understanding of the reaction mechanisms accompanied by careful selection of an analytical condition for the most effective isomeric ion formation.

References

1. Horning, S. R.; Bier, M. E.; Cooks, R. G.; Brusini, G.; Traldi, P.; Guiotto, A.; Rodighiero, P. *Biomed. Environ. Mass Spectrom.* **1989**, 18, 920.
2. McLafferty, F. W. *Anal. Chem.* **1962**, 34, 16.
3. Yeo, N. H.; Williams, D. H. *Chem. Commun.* **1970**, 886.
4. Proctor, C. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1983**, 18, 193.
5. Bass, L. M.; Bowers, M. T. *Org. Mass Spectrom.* **1982**, 17, 229.
6. Kuck, D. *Mass Spec. Reviews* **1990**, 9, 187.
7. Shin, S. K.; Han, S.-J.; Kim, B. *Int. J. Mass Spectrom. Ion Processes* **1996**, 157/158, 345.
8. Kim, B.; Shin, S. K. *J. Chem. Phys.* **1997**, 106, 1411.
9. Lifshitz, C.; Levin, I.; Kababia, S.; Dunbar, R. C. *J. Phys. Chem.* **1991**, 95, 1667.
10. Dunbar, R. C.; Lifshitz, C. *J. Chem. Phys.* **1991**, 94, 3542.
11. Dunbar, R. C.; Honovich, J. P.; Asamoto, B. *J. Phys. Chem.* **1988**, 92, 6935.
12. Lin, C. Y.; Dunbar, R. C. *J. Phys. Chem.* **1994**, 98, 1369.
13. Olesik, S.; Baer, T.; Morrow, J. C.; Ridal, J. J.; Buschek, J.; Holmes, J. L. *Org. Mass Spectrom.* **1989**, 24, 1008.
14. Mabud, Md. A.; Ast, T.; Verma, S.; Jiang, Y. X.; Cooks, R. G. *J. Am. Chem. Soc.* **1987**, 109, 7597.
15. Hayward, M. J.; Mabud, Md. A.; Cooks, R. G. *J. Am. Chem. Soc.* **1988**, 110, 1343.
16. Mabud, Md.; Ast, T.; Cooks, R. G. *Org. Mass Spectrom.* **1987**, 22, 418.
17. Vincenti, M.; Horning, S. R.; Cooks, R. G. *Org. Mass Spectrom.* **1988**, 23, 585.
18. Jo, S.-C.; Augusti, R.; Green, J.; Cooks, R. G. (*Unpublished*).
19. Shen, J. W.; Grill, V.; Evans, C.; Cooks, R. G. *J. Mass Spectrom.* **1999**, 34, 354.
20. Denault, J. W.; Evans, C.; Koch, K. J.; Cooks, R. G. *Anal. Chem.* **2000**, 72, 5798.