Supplementary Material

Energy- and Time-Dependent Branching to Competing Paths in Coupled Unimolecular Dissociations of Chlorotoluene Radical Cations[†]

Jongcheol Seo,[‡] Seung Joon Kim,[§] and Seung Koo Shin[‡,*]

[‡]*Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea*
[*]*E-mail: skshin@postech.ac.kr*
[§]*Department of Chemistry, Hannam University, Daejeon 300-791, Korea*
Received September 25, 2013, Accepted October 13, 2013

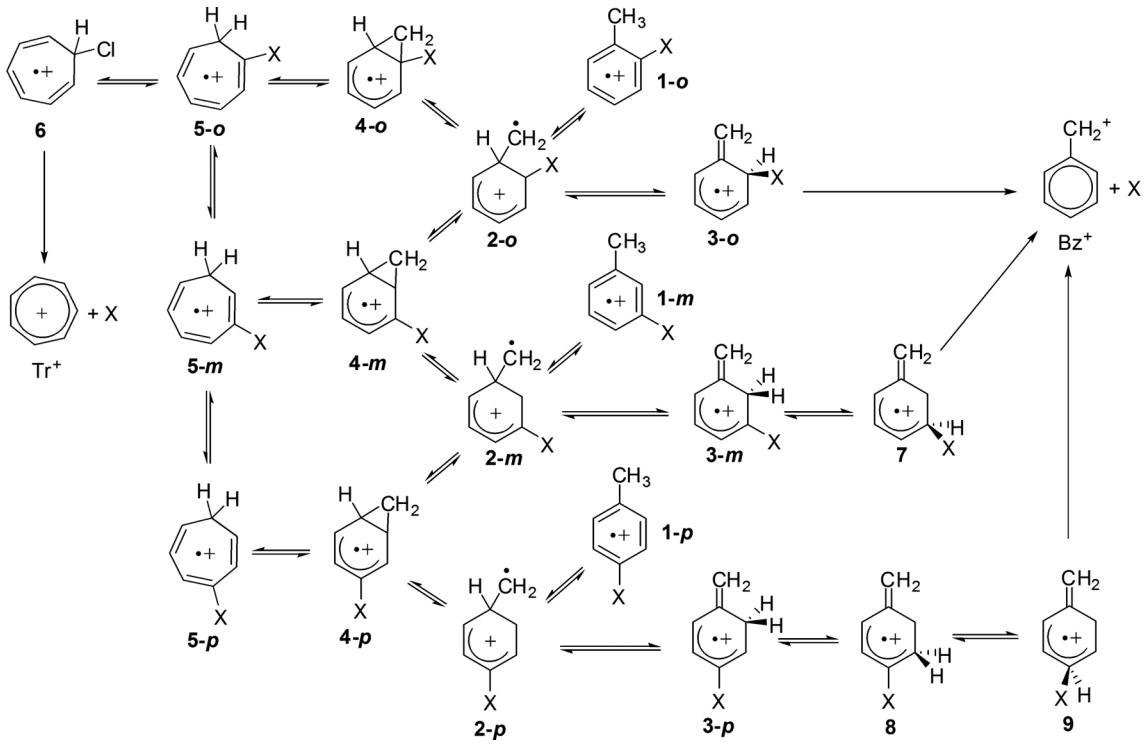

Figure S1. The proposed mechanism for the unimolecular dissociation of the *o*-, *m*-, and *p*-halotoluene radical cations ($C_7H_7X^{+\bullet}$) denoted by **1-*x*** (*x* = *o*, *m*, and *p*). The benzylium and tropylium product ions are denoted by Bz^+ and Tr^+, respectively. X = Cl, in the present study.

[†]This paper is to commemorate Professor Myung Soo Kim's honourable retirement.

Table S1. Relative Energies of the Local Minima and the Transition States on the Dissociation Pathways of *o*-, *m*-, and *p*-Chlorotoluene Radical Cations at 0 K[a]

o-isomer		*m*-isomer		*p*-isomer	
transient species	relative energy ΔE (kcal mol^{-1})	transient species	relative energy ΔE (kcal mol^{-1})	transient species	relative energy ΔE (kcal mol^{-1})
1-*o*	0.0	**1-*m***	0.0	**1-*p***	0.0
o-tolyl + Cl	75	*m*-tolyl + Cl	77	*p*-tolyl + Cl	82
TS1	38	TS6	41	TS12	40
2-*o*	36	**2-*m***	40	**2-*p***	38
benzylium dissociation channel					
2-*o*	36	**2-*m***	40	**2-*p***	38
TS2	41	TS7	41	TS13	37
3-*o*	18	**3-*m***	7.3	**3-*p***	14
TSB-o	32	TS9	37	TS15	34
Bz+ + Cl	34	**7**	33	**8**	24
		TSB-*m*	33	TS16	36
		Bz^+ + Cl	34	9	25
				TSB-p	36
				Bz^+ + Cl	37
tropylium dissociation channel					
2-*o*	36	**2-*m***	40	**2-*p***	38
TS3	38	TS8	43	TS14	38
4-*o*	30	**4-*m***	21	**4-*p***	27
TS5	47	TS10	34	TS17	33
6	23	**5-*m***	20	**5-*p***	20
TST	26	TS11	45	TS18	45
Tr^+ + Cl	26	**5-*o***	16	**5-*m***	22
		TS5	47	TS11	48
		6	23	**5-*o***	18
		TST	26	TS5	50
		Tr^+ + Cl	26	**6**	26
				TST	29
				Tr^+ + Cl	29
coupling processes					
2-*o*	36	**2-*m***	40	**4-*p***	27
TSOM	37	TSMP	42	TSMP	45
4-*m*	20	**4-*p***	24	**2-*m***	43
		4-*m*	21		
		TSOM	38		
		2-*o*	37		

[a]Relative energies are with respect to the reactant **1-*x*** (*x* = *o*, *m*, and *p*)

Full Citation of Reference 14

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.