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Theoretical Study on Chlorine and Hydrogen Shift in Cycloheptatriene and Cyclopentadiene Derivatives

Toshiya Okajima*

Department of Chemistry, Faculty of Culture and Education, Saga University, Honjo 1, Saga 840-8502, Japan

Kimiaki Imafuku*

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

okajimat@cc.saga-u.ac.jp

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The transition structures (TSs) for chlorine 1,7-shift and 1,5-shift in 1,7,7-trichlorocycloheptatriene (**1**) and those of chlorine 1,5-shifts in 1,5,5-trichlorocyclopentadiene (**3**) and 1,2,5-trichloro-1,3-pentadiene (**5**) derivatives have been located with density functional theory (DFT) at the Becke3LYP/6-311G** [and Becke3LYP/6-311+G**] level. The calculational results were compared with those for corresponding hydrogen shifts in nonsubstituted molecules (cycloheptatriene (**2**), cyclopentadiene (**4**), and 1,3-pentadiene (**6**)). The following points were clarified: (1) The activation energy ($\Delta E^{\ddagger}$) for chlorine 1,7-shift in **1** was evaluated to be only +50.1 [+49.2] kJ/mol, which is smaller than that (+69.9 [+68.3]) for a 1,5-shift, supporting the theory that the conversion between two equivalent **A** and **A′** proceeds through a TS for direct chlorine 1,7-shift (Figure 1), rather than through a TS for a 1,5-shift (Figure 2). (2) The considerable amount of charge separation between a migrating chlorine atom (Cl^m) and a seven-membered ring (−0.53 and +0.47 for Merz−Singh−Kollman scheme) occurs in a chlorine 1,7-shift, which is in good contrast to the result that the migrating hydrogen atom (H^m) for a 1,7-shift in cycloheptatriene (**2**) carries almost no charge (Figure 3). This large charge separation can stabilize the TS for the chlorine 1,7-shift pathway. (3) The $\Delta E^{\ddagger}$ values for suprafacial hydrogen 1,7-shift in **2** are quite large (+288.0 [+284.8] kJ/mol), much larger than that (+166.8 [+167.0]) for a 1,5-shift in **4** which is orbital symmetrically allowed (Figure 3). The calculation suggests that the chlorine 1,7-shift in **1** occurs easily at room temperature (actually observed experimentally) by proceeding via concerted suprafacial 1,7-shift through the zwitterionic TS with the significant assistance of Coulomb interaction between charged fragments (negatively charged chlorine atom and positively charged tropylium ring), rather than via a suprafacial 1,5-sigmatropic pathway. Other cases studied in this paper showed usual results predicted by orbital symmetrical consideration.

Introduction

A thermal [1,*n*]-sigmatropic rearrangement was systematized by Woodward and Hoffman as the well-known rule (W-H rule) on the basis of the conservation of orbital symmetry.[1] In the W-H rule, suprafacial 1,5-shift in polyenes is thermally allowed, and 1,7-shift forbidden. Many studies have been reported on 1,5-sigmatropic shift in 1,3-pentadiene, cyclopentadiene, and cycloheptatriene derivatives. It has, thus, been well-known that hydrogen 1,5-shifts in 1,3-pentadiene, 1,3-cycloheptadiene, and cycloheptatriene derivatives occur at relatively low temperatures.[2−6] Theoretical calculations have also presented low activation energies ($\Delta E^{\ddagger}$) for the 1,5-shift in these compounds.[7−10] For example, Houk and co-workers reported that the activation energy ($\Delta E^{\ddagger}$) for the hydrogen 1,5-shift in 1,3-pentadiene was evaluated to be +143 kJ/mol at RMP2/6-311G**//RMP2/6-31G*,[8e] which is in good agreement with experimental results (+148.2 kJ/mol in the temperature range 185−205 °C[4d]). Koch and co-workers reported the chlorine 1,5-shift in 5-chloro-1,3-pentadiene to be +173 kJ/mol.[9] For this discussion, a simple extension of W-H's theory predicts that a suprafacial 1,7-shift does not proceed thermally. Actually, few reports have been found on thermal suprafacial 1,7-shift.

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[1] (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511. (b) Roth, W. R. *Chimia* **1966**, *20*, 229. (c) Woodward, R. B.; Hoffmann. R. *The Conservation of Orbital Symmetry*; Verlag Chemie GmbH/Academic Press: Winheim/Bergstr., 1970. (d) Hoffmann, R.; Woodward, R. B. *Acc. Chem. Res.* **1968**, *1*, 17. (e) Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 103. (f) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. (g) Gilchrist, T. L.; Storr, R. C. *Organic Reactions and Orbital Symmetry*; Cambridge University Press: New York, 1972. (h) Fleming. I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: 1976. (i) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

[2] Hydrogen 1,5-shift in cyclopentadiene: (a) McLean, S.; Haynes, P. *Tetrahedron* **1965**, *21*, 2329. (b) de Haan, J. W.; Kloosterziel, H. *Rec. Trav. Chim.* **1968**, *87*, 298.

[3] Chlorine 1,5-shift in cyclopentadiene: Mikhailov, I. E.; Dushenko, G. A.; Kisin, A. V.; Mugge, C.; Zschunke, A.; Minkin, V. I. *Mendeleev Commun.* **1994**, 85.

[4] Hydrogen 1,5-shift in 1,3-pentadiene: (a) Wolinsky, J.; Chollar, B.; Baird, M. D. *J. Am. Chem. Soc.* **1962**, *84*, 2775. (b) Ellis, R. J.; Frey, H. M. *Proc. Chem. Soc.* **1964**, 221. (c) Frey, H. M.; Ellis, R. J. *J. Chem. Soc.* **1965**, 4770. (d) Roth, W. R.; Konig, J. *Liebigs Ann. Chem.* **1966**, *699*, 24. (e) Frey, H. M.; Pope, B. M. *J. Chem. Soc. A* **1966**, 1701. (f) Roth, W. R.; Konig, J.; Stein, K. *Chem. Ber.* **1970**, *103*, 426. Cf: Kwart, H.; Brechbiel, M. W.; Acheson, R. M.; Ward, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4671.

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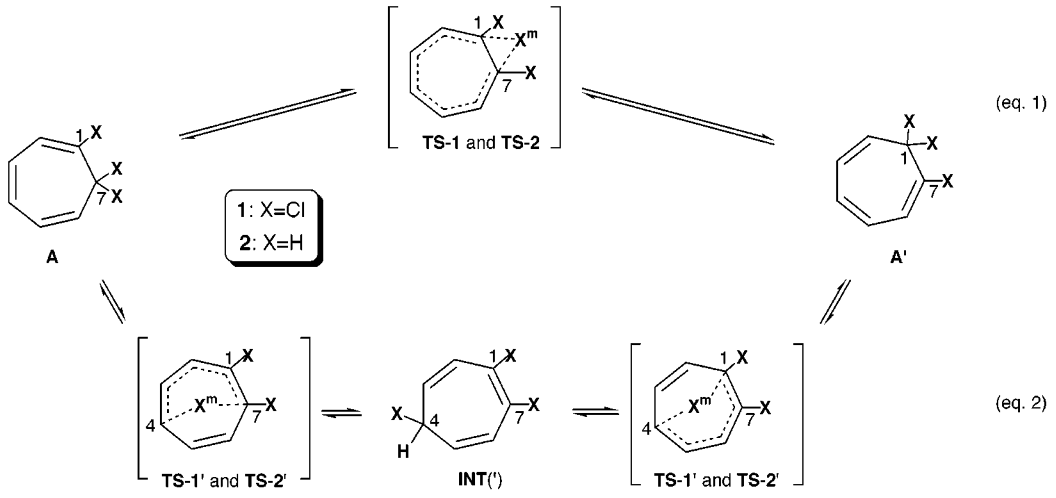
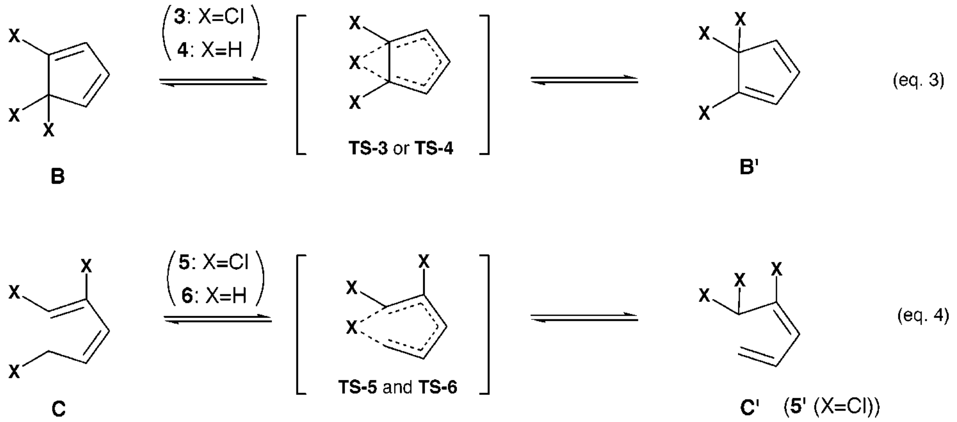
Scheme 1



Scheme 2



Recently, however, we have found that ^{1}H NMR data (CDCl$_3$, δ, TMS) of 1,7,7-trichlorocycloheptatriene (**1**) shows only three sets of signals [6.34 ppm (d, $J = 9.9$ Hz), 6.02 (dd, 9.9, 7.7 Hz), and 5.54 (t, 7.7 Hz)].[11] This experimental result suggests that the thermal chlorine atom transfer occurs easily between the two equivalent structures 1,7,7-trichloro- and 1,1,7-trichlorocycloheptatriene **A** and **A′**, respectively (Scheme 1), at room temperature. We can postulate two plausible mechanisms to interpret this interesting phenomenon. One is chlorine suprafacial 1,7-shift (eq 1) and the other is successive chlorine suprafacial 1,5-shift (eq 2). Since suprafacial 1,7-shift is thermally forbidden and the 1,5-shift is allowed[1] by the W-H rule, the latter pathway is likely to be predominant. To judge the predominancy between these two pathways, theoretical calculation was performed in this study. The results were compared with the results for chlorine and/or hydrogen shifts for chloro-substituted and parent cycloheptatriene, cyclopentadiene, and 1,3-pentadiene derivatives (Scheme 2).

Method

The calculations were performed using the GAUSSIAN 98 programs[12] with density functional theory (DFT). Geometries of all stationary points including transition structures (TSs) were optimized by utilizing the gradient method without any geometrical constraint at the Becke3LYP/6-311G** [Becke3LYP/6-311G**] level.[13] Energetics were investigated at the Becke3LYP/6-311G**//Becke3LYP/6-311G** [Becke3LYP/6-311+G**//Becke3LYP/6-311+G**] level. For stationary points,

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(5) Hydrogen 1,5-shift in 1,3,5-cycloheptatriene: (a) Ter Borg, A. P.; Kloosterziel, H.; van Meurs, N. *Proc. Chem. Soc.* **1962**, 359. (b) Ter Borg, A. P.; Kloosterziel, H. *Recl. Trav. Chim.* **1963**, *82*, 741. (c) Ter Borg, A. P.; Kloosterziel, H.; van Meurs. N. *Recl. Trav. Chim.* **1963**, *82*, 717. (d) Ter Borg, A. P.; Kloosterziel, H. *Recl. Trav. Chim.* **1965**, *84*, 245. (e) Ter Borg, A. P.; Razenberg, E.; Kloosterziel, H. *Recl. Trav. Chim.* **1965**, *84*, 1230. (f) Egger, K. W. *J. Am. Chem. Soc.* **1967**, *89*, 3688. (g) Ter Borg, A. P.; Kloaaterziel, H.; Westphal. Y. L. *Recl. Trav. Chim.* **1967**, *86*, 474. (h) Pomerantz, M.; Gruber. G. W. *J. Org. Chem.* **1968**, *33*, 4501. (i) Ter Borg, A. P.; Kloosterziel. H. *Recl. Trav. Chim.* **1969**, *88*, 266. (j) Gruber, G. W.; Pomerantz, M. *Tetrahedron Lett.* **1970**, *43*, 3755. (k) Pomerantz, M.; Ross, A. S.; Gruber, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 1403. (l) Pomerantz, M.; Fink, R. *J. Org. Chem.* **1977**, *42*, 2788.

(6) Chlorine 1,5-shift in cycloheptatriene: (a) Looker, J. J. *J. Org. Chem.* **1972**, *37*, 1059. (b) Pomerantz, M.; Fink, R. *J. Org. Chem.* **1977**, *42*, 2788.

(7) Hydrogen 1,5-shift in cyclopentadiene: (calcn.) de Dobbelaere, J. R.; de Haan, J. W.; Buck, H. M.; Visser, G. J. *Theor. Chim. Acta* **1973**, *31*, 95.

(8) Hydrogen 1,5-shift in 1,3-pentadiene: (calcn.) (a) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7185. (b) Dewar, M. J. S.; Mertz, K. M., Jr.; Stewart, J. P. *J. Chem. Soc., Chem. Commun.* **1985**, 166. (c) Dormans, G. J. M.; Buck, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 3253. (d) Dormans, G. J. M.; Buck, H. M. *J. Mol. Struct. (THEOCHEM)* **1986**, *136*, 121. (e) Jensen, F. J.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139.

(9) Chlorine 1,5-shift in 5-chloro-1,3-pentadiene: (calcn.) Koch, R.; Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 6809.

(10) Hydrogen 1,5-shift in 1,3,5-cycloheptatriene: (calcn.) (a) Weth, E.; Dreiding, A. S. *Proc. Chem. Soc.* **1964**, 59. (b) de Dobbelaere, J. R.; van Zeeventer, E. L.; de Haan, J. W.; Buck, H. M. *Theor. Chim. Acta* **1975**, *38*, 241.

(11) (a) Funamizu. M. Ph.D. Thesis, Tohoku University, 1965. (b) Imafuku, K.; Matsunaga, Y. 13th Symposium on Fundamental Organic Chemistry, Nagoya, November 1−3, 1996.

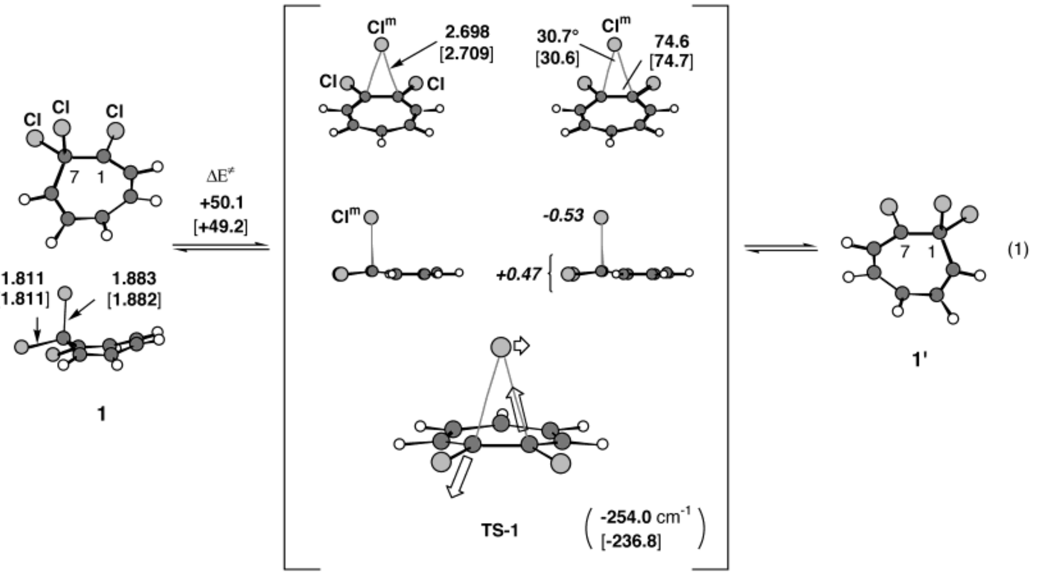

Figure 1. Becke3LYP/6-311G** transition structure (**TS-1**) for chlorine 1,7-shift in 1,7,7-trichlorocycloheptatriene (**1**). Atomic distances are in angstroms and angles in degrees. Energies at Becke3LYP/6-311G** are in kJ/mol. The values in italics are the charges calculated by Merz−Singh−Kollman scheme. The value in parentheses is single imaginary frequency. The parameters at Becke3LYP/6-311+G** are also shown in brackets. The normal mode eigenvectors for single imaginary frequency are shown by arrows.

an energy minimum and maximum point (TS) were characterized by no and one negative eigenvalue (that is, a single imaginary frequency) of its Hessian matrix, respectively. All TSs were authorized by IRC calculation to be the concerted TSs connecting the corresponding ground-state structures, which are shown in Schemes 1 and 2. Scheme 1 consists of two pathways for chlorine and hydrogen migrations in the cases of 1,7,7-trichlorocycloheptatriene (**1**) and parent 1,3,5-cycloheptatriene (**2**), where eq 1 is the one for a 1,7-shift and eq 2 for a 1,5-shift. Scheme 2 consists of the pathways for 1,5-shifts in cyclopentadienes (**3** and **4**) and in 1,3-pentadienes (**5** and **6**).

In this paper, the words "allowed" and "forbidden" are used for *charge-controlled* chlorine migration in **1**, despite the peculiar words originally used for the *orbital-controlled* migration reaction (established as W-H rule).

Results and Discussion

We have successfully located the transition structure (TS) (**TS-1**) for intramolecular chlorine suprafacial 1,7-shift of **1** by using density functional theory (DFT) with Becke3LYP/6-311G** and Becke3LYP/6-311+G** levels, which is shown in Figure 1. **TS-1** has C_s symmetric geometry with a C⋯$\mathrm{Cl^m}$ atomic distance of 2.698 Å [2.709 at Becke3LYP/6-311+G**] and a $\mathrm{C^1 \cdots Cl^m \cdots C^7}$ bond angle of 30.7° [30.6] (Table 1, Part 1). A population analysis using the Merz−Singh−Kollman (MSK) scheme indicates that the migrating chlorine atom ($\mathrm{Cl^m}$) carries a considerable amount, −0.53 (−0.55 for Mulliken's population analysis), of negative charge (Table 2). The seven-membered ring in **TS-1** is almost planar and carries a positive charge of +0.47 (+0.45). These partial charges suggest a large contribution of Coulomb interaction between anionic chlorine and the planar tropylium ring to stabilize the TS. Other methods, CHelp, CHelpG, and NBO analysis, were applied for the population analysis to confirm the charge effect. As shown in Table 2, all methods to evaluate atomic charge predict that migrating chlorine carries a negative charge of −0.5 to −0.6 at **TS-1**. The activation energy ($\Delta E^{\ddagger}$) for **TS-1** was calculated to be only +50.1 [+49.2] kJ/mol, predicting rapid 1,7-shift of chlorine atom at room temperature (Table 3). This calculational result is consistent with ^{1}H NMR data. The geometrical parameters optimized at both Becke3LYP/6-311G** and Becke3LYP/6-311+G** levels quite resemble each other. The TS for a 1,5-shift could also be located (**TS-1′**); the geometry is shown in Figure 2 and the structural parameters are shown in Table 1, Part 2. In **TS-1′**, the migrating chlorine also has a negative charge of −0.58 (MSK) at Becke3LYP/6-311G**. The atomic distances between $\mathrm{Cl^m}$ and two carbon atoms at Becke3LYP/6-311G** are 2.929 Å ($\mathrm{Cl^m \cdots C^7{-}Cl}$) and 2.992 Å ($\mathrm{Cl^m \cdots C^4{-}H}$) and the angle for $\mathrm{C^4 \cdots Cl^m \cdots C^7}$ is 61.2°. The calculated $\Delta E^{\ddagger}$ for the 1,5-shift is, however, considerably larger, +69.9 (+68.3) kJ/mol, than that (+50.1 [+49.2]) for **TS-1**. This result, unexpectedly, indicates the predominancy of a suprafacial 1,7-shift in the intramolecular chlorine migrating mechanism in **1** (Table 3). In **TS-1′**, the seven-membered ring is bent into the boat form by the bridging of $\mathrm{Cl^m}$ between two carbon atoms at the 4- and 7-position (transannular 1,5-chlorine shift). The bent tropylium structure must reduce the

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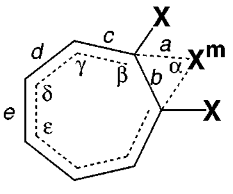
(12) Gaussian 98, Revision A.4. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(13) (a) Hu, C.-H.; Chong, D. P. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Editor-in-chief; John-Wiley & Sons: Chichester, 1998; pp 664−689. (b) Krishman, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (c) Becke, A. D. *Phys. Rev.* **1988**, *A37*, 785. (d) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (e) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785. (f) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (g) Becke. A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (h) Stevens, P. J.; Delvin, F. J.; Chablowski, C. F.; Frish. M. J. *J. Phys. Chem.* **1994**, *80*, 11623.

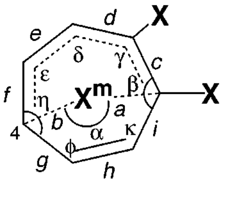
Table 1



TS-1 (X=Cl)
TS-2 (X=H)

Table 1-1 Some Becke3LYP/6-311G** [Becke3LYP/6-311+G**] geometrical parameters for **TS-1** and **TS-2**.

	a (Å)	*b*	*c*	*d*	*e*
TS-1	2.698 [2.709]	1.430 [1.430]	1.400 [1.402]	1.388 [1.388]	1.392 [1.392]
TS-2	1.502 [1.490]	1.414 [1.413]	1.425 [1.428]	1.388 [1.389]	1.405 [1.406]
	α (°)	β	γ	δ	ε
TS-1	30.7 [30.6]	126.8 [126.8]	130.0 [129.9]	129.5 [129.5]	126.8 [126.8]
TS-2	56.0 [56.6]	128.9 [128.9]	126.0 [125.9]	131.5 [131.4]	126.0 [126.0]



TS-1' (X=Cl)
TS-2' (X=H)

Table 1-2 Some Becke3LYP/6-311G** [Becke3LYP/6-311+G**] geometrical parameters for **TS-1'** and **TS-2'**.

	a (Å)	*b*	*c*	*d*	*e*
TS-1'	2.929 [2.961]	2.992 [3.020]	1.415 [1.415]	1.390 [1.391]	1.392 [1.392]
TS-2'	1.442 [1.443]	= *a*	1.421 [1.421]	1.395 [1.396]	= *d*
	α (°)	β	γ	δ	ε
TS-1'	61.2 [60.8]	124.0 [124.5]	126.0 [126.0]	126.0 [126.3]	128.2 [128.3]
TS-2'	121.6 [121.5]	117.2 [117.3]	121.5 [121.5]	119.7 [119.7]	= γ
	f	*g*	*h*	*i*	
TS-1'	1.389 [1.389]	1.414 [1.412]	1.363 [1.366]	1.424 [1.421]	
TS-2'	= *c*	1.500 [1.500]	1.330 [1.332]	= *g*	
	η	φ	κ		
TS-1'	125.5 [125.7]	125.3 [125.5]	125.9 [126.3]		
TS-2'	= β	113.3 [113.3]	= φ		

Table 2. Atomic Charges on Migratong Chlorine (TS-1, TS-1′, TS-3, and TS-5) and Hydrogen Atoms (TS-2, TS-2′, TS-4, and TS-6) Calculated at Becke3LYP/6-311G and at Becke3LYP/6-311+G** Levels**

	TS-1	TS-1′	TS-2	TS-2′	TS-3	TS-4	TS-5	TS-6
Merz−Singh−Kollman	−0.53	−0.58	−0.03	−0.02	−0.25	+0.13	−0.37	+0.18
CHelp	−0.54	−0.56	−0.05	−0.17	−0.29	+0.09	−0.42	−0.10
CHelpG	−0.54	−0.60	−0.05	−0.10	−0.28	+0.10	−0.40	+0.08
NBO	−0.58	−0.66	+0.12	+0.24	−0.20	+0.33	−0.40	+0.24
Mulliken	−0.55	−0.62	−0.01	−0.02	−0.19	+0.18	−0.37	+0.15
			Becke3LYP/6-311+G**					
Merz−Singh−Kollman	−0.50	−0.57	−0.01	−0.02	−0.24	+0.12	−0.35	+0.20
Mulliken	−0.56	−0.57	+0.06	+0.19	−0.27	+0.21	−0.35	+0.19

Table 3. Activation Energies ($\Delta E^{\ddagger}$, kJ/mol) Activation Entropies ($\Delta S^{\ddagger}$, J/mol K), Free Energies of Activation ($\Delta G^{\ddagger}$, kJ/mol), Zero-Point Energies ([ZPE], kJ/mol),[a] and Imaginary Frequencies (cm^{-1}) in Parentheses at Becke3LYP/6-311G and Becke3LYP/6-311+G** Levels**

	TS-1	TS-1′	TS-2	TS-2′	TS-3	TS-4	TS-5	TS-6
			Becke3LYP/6-311G**					
$\Delta E^{\ddagger}$	+50.1	+69.9	+288.0	+166.8	+114.4	+116.2	+158.6	+167.7
$\Delta E^{\ddagger}$ corrected by ΔZPE	+52.5	+72.6	+307.7	+179.6	+118.7	+125.0	+163.1	+175.8
$S^{\ddagger}$	405.3	408.9	318.8	304.7	362.9	274.4	388.3	289.6
[$\Delta S^{\ddagger}$]	[−0.7]	[+2.9]	[+3.1]	[−10.9]	[−4.9]	[−4.9]	[−20.5]	[−26.9]
$\Delta G^{\ddagger\ b}$	+47.9	+66.3	+268.0	+155.6	+111.0	+107.9	+158.8	+163.7
ZPE	257.4	257.1	315.7	322.2	165.1	233.3	223.3	288.1
[ΔZPE]	[−2.4]	[−2.7]	[−19.7]	[−12.8]	[−4.3]	[−8.8]	[−4.5]	[−8.1]
imaginary frequencies	(−254.0)	(−192.0)	(−3065.0)	(−1503.0)	(−454.1)	(−1216.1)	(−318.8)	(−1546.3)
			Becke3LYP/6-311+G**					
$\Delta E^{\ddagger}$	+49.2	+68.3	+284.8	+167.0	−	+115.2	−	+167.3
$\Delta G^{\ddagger}$	+46.9	+64.6	+264.9	+155.7	−	+107.0	−	+163.4
	(−236.8)	(−181.2)	(−3063.7)	(−1505.4)		(−1212.0)		(−1547.1)

[a] The energy differences ($\Delta E^{\ddagger}$, $\Delta S^{\ddagger}$, and ΔZPE) are those between the energies of TSs and those of GSs (for example, $\Delta E^{\ddagger} = E_{TS} - E_{GS}$).
[b] $\Delta G^{\ddagger}$ were calculated at 298.15 K.

stabilization of the TS. For the case of the dibenzo[*a*,*d*]-cycloheptene derivatives, Looker has reported that a concerted 1,5-shift of chlorine[14] appears to be a more plausible mechanism than that through the ionic intermediate.[15] The $\Delta E^{\ddagger}$ for chlorine 1,5-shift in 7,7-dichlorocycloheptatriene was evaluated to be +79.7 kJ/mol at the Becke3LYP/6-311G** level and the negative charge on migrating chlorine is calculated to be −0.58 (MSK) and −0.63 (Mulliken).[16] In the pathway through **TS-1′**, an intermediate (1,2,5-trichlorocycloheptatriene, **INT**) having a boatlike conformation for the seven-membered ring could be located.

For the chlorine 1,7-shift in **1**, IRC calculation reveals that the potential energy surface for the chlorine 1,7-shift

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(14) Looker, J. J. *J. Org. Chem.* **1972**, *37*, 1059.
(15) Looker, J. J. *J. Org. Chem.* **1966**, *31*, 3599.
(16) van Eis, M. J.; van der Linde, B. S. E.; de Kanter, F. J. J.; de Wolf, W. H.; Bickelhaupt, F. *J. Org. Chem.* **2000**, *65*, 4348.

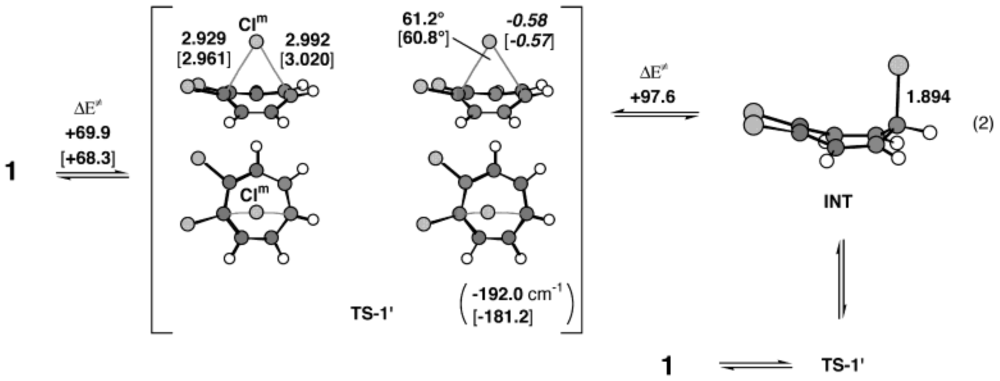

Figure 2. Becke3LYP/6-311G** transition structure (**TS-1′**) and intermediate (**INT**) for chlorine 1,5-shift in 1,7,7-trichlorocycloheptatriene (**1**). Atomic distances are in angstroms and angles in degrees. Energies at Becke3LYP/6-311G** are in kJ/mol. The values in italics are the charges calculated by Merz−Singh−Kollman scheme. The value in parentheses is single imaginary frequency. The parameters at Becke3LYP/6-311+G** are also shown in brackets.

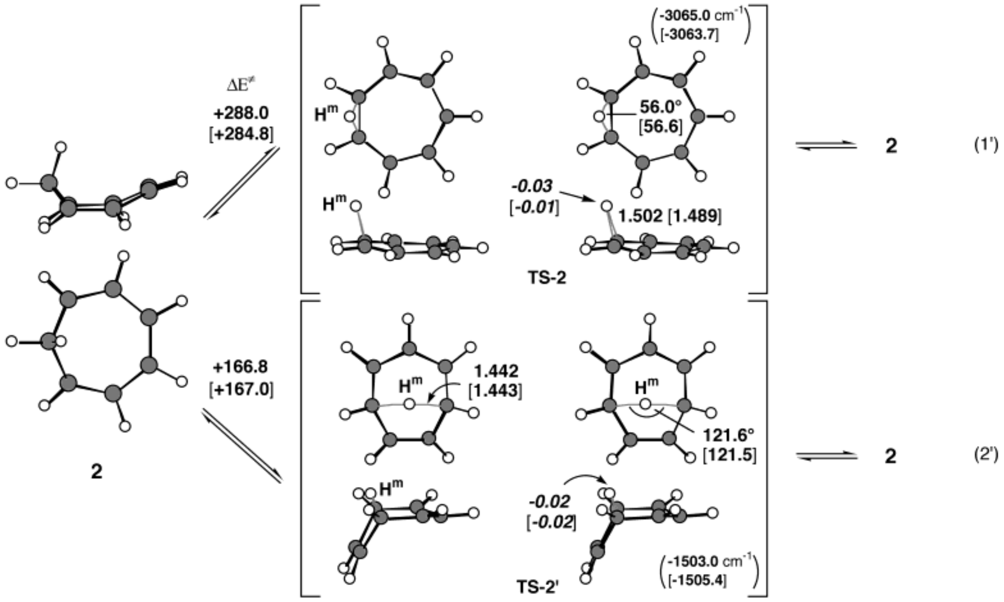

Figure 3. Becke3LYP/6-311G** transition structures (**TS-2** for 1,7-shift and **TS-2′** for 1,5-shift) for hydrogen migration in trichlorocycloheptatriene (**2**). Atomic distances are in angstroms and angles in degrees. Energies at Becke3LYP/6-311G** are in kJ/mol. The values in italics are the charges calculated by Merz−Singh−Kollman scheme. The value in parentheses is single imaginary frequency. The parameters at Becke3LYP/6-311+G** are also shown in brackets.

directly connects two equivalent cycloheptatriene structures (**A** and **A′** in Scheme 1). On the other hand, it is experimentally known that 1,5-shift occurs easily via a suprafacial process.[1] The low $\Delta E^{\ddagger}$ for the orbitally forbidden 1,7-shift compared to the allowed 1,5-shift suggests that the 1,7-chlorine shift of **1** proceeds with considerable assistance of Coulomb interaction between the migrating anionic chlorine atom and a cationic tropylium carbon atom.

According to the rule of the conservation of orbital symmetry, a 1,7-sigmatropic shift can be predicted to proceed through the antarafacial mode (allowed) rather than the suprafacial mode (forbidden) in the thermal condition.[1] In Figure 3, hydrogen migrating TSs both for 1,7- (**TS-2**) and for 1,5-shift (**TS-2′**) in the parent 1,3,5-cycloheptatriene (**2**) are shown.[17] **TS-2** has C_s symmetric geometry and the atomic distance between $C\cdots H^m$ is 1.502 [1.490] Å and the angle of $C^1\cdots H^m\cdots C^7$ is 56.0° [56.6] at Becke3LYP/6-311G** [Becke3LYP/6-311+G**] (Table 1, Parts 1 and 2). Although the seven-membered ring in **TS-2** is almost planar and looks like a stable tropylium ion structure, the migrating hydrogen atom carries no charge, which is quite different from the case for the 1,7-shift in **1** (Cl^m in **TS-1** is considerably negatively charged (−0.53)). The extremely high $\Delta E^{\ddagger}$ (+288.0 [+284.8] kJ/mol) for **TS-2** (X = H in Scheme 1 (eq 1)) and much lower $\Delta E^{\ddagger}$ (+166.8 [+167.0] kJ/mol) for **TS-2′** (eq 2) are consistent with the fact that thermal suprafacial 1,7-sigmatropic shift is an orbitally forbidden process and the suprafacial 1,5-shift is an allowed one. Those $\Delta E^{\ddagger}$ values are in good agreement with Donovan's work.[17] Since the hydrogen atom has a much smaller potency to carry a negative charge than chlorine, the assistance of Coulomb interaction cannot be expected. Thus, the hydrogen 1,7-shift proceeds, actually, with high $\Delta E^{\ddagger}$ with no assistance of Coulomb interaction (Figure 3 and Table 2).

Figure 4 shows two Becke3LYP/6-311G** TSs for the reactions of cyclopentadiene derivatives, **TS-3** for the chlorine 1,5-shift in 1,5,5-trichlorocyclopentadiene (**3**) and

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[17] Donovan, W. H.; White, W. E. *J. Org. Chem.* **1996**, *61*, 969.

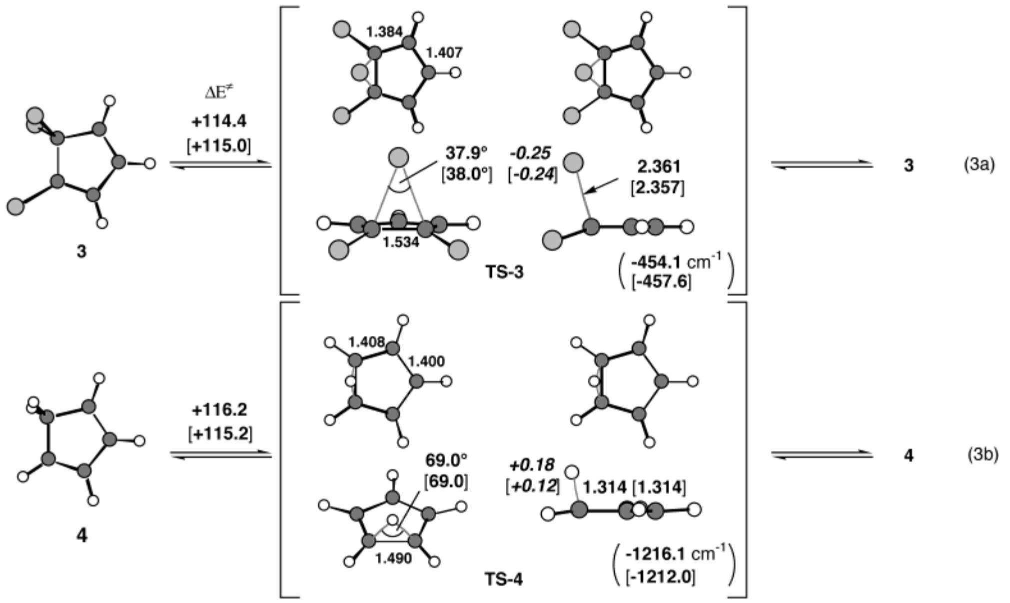

Figure 4. Becke3LYP/6-311G** transition structures (**TS-3** for chlorine 1,5-shift in **3** and **TS-4** for hydrogen 1,5-shift in **4**). Atomic distances are in angstroms and angles in degrees. Energies at Becke3LYP/6-311G** are in kJ/mol. The values in italics are the charges calculated by Merz−Singh−Kollman scheme. The value in parentheses is single imaginary frequency. The parameters at Becke3LYP/6-311+G** are also shown in brackets.

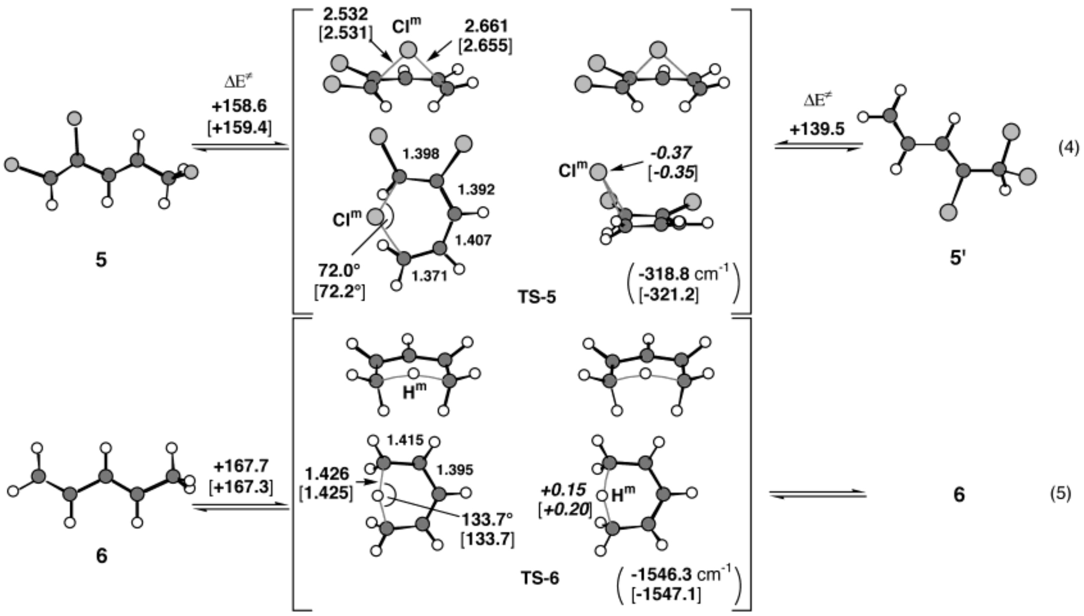

Figure 5. Becke3LYP/6-311G** transition structures (**TS-5** for chlorine 1,5-shift of 1,2,5-trichloro-1,3-pentadiene (**5**) (4,5,5-trichloro-1,3-pentadiene (**5′**)) and **TS-6** for 1,3-pentadiene (**6**). Atomic distances are in angstroms and angles in degrees. Energies at Becke3LYP/6-311G** are in kJ/mol. The values in italics are the charges calculated by Merz−Singh−Kollman scheme. The value in parentheses is single imaginary frequency. The parameters at Becke3LYP/6-311+G** are also shown in brackets.

TS-4 for the hydrogen 1,5-shift in cyclopentadiene (**4**). The $\Delta E^{\ddagger}$ values for **TS-3** and **TS-4** are almost the same, +114.4 [+115.0] kJ/mol and +116.2 [+115.2] kJ/mol, respectively. Interestingly, the charges on migrating atoms are −0.25 (chlorine) for **TS-3** and +0.13 (hydrogen) for **TS-4**, though the five-membered cyclopentadiene ring has the tendency to become negatively charged to give a cyclopentadienyl anion. Therefore, the electronegative chlorine atom (Cl^m) carries a much smaller amount of negative charge (−0.25) than that (−0.53) growing on Cl^m in **TS-1**. Clearly, this result supports a smaller contribution of Coulomb interaction to stabilize **TS-3** ($\Delta E^{\ddagger}$ changed from +50.1 kJ/mol for suprafacial 1,7-shift in **TS-1** to +114.4 for 1,5-shift in **TS-3**). These calculational results imply that 1,5-shifts in cyclopentadienes proceed fundamentally under orbitally controlled conditions (consistent with the prediction of W-H rule) with little contribution of Coulomb stabilization. Figure 5 shows TSs in the cases of **TS-5** for chlorine 1,5-shift in 1,2,5-trichloro-1,3-pentadiene (**5**) and **TS-6** for hydrogen 1,5-shift in 1,3-pentadiene (**6**). The $\Delta E^{\ddagger}$ values resemble each other, +158.6 [+159.4] kJ/mol and +167.7 [+167.3] kJ/mol, respectively, and are larger than those obtained for the reactions of cyclopentadienes (**3** and **4**). This could be due to the chain structures of **5** and **6**, which need to be cyclized before the 1,5-sigmatropic shift in order to bring

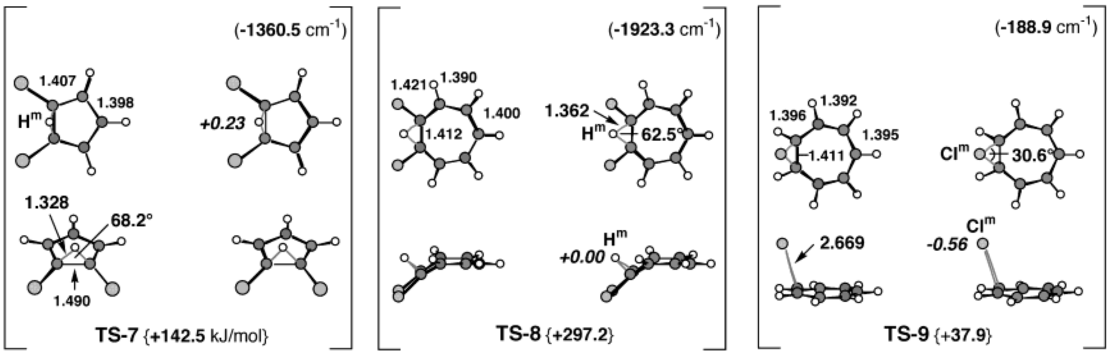

Figure 6. Becke3LYP/6-311G** transition structures for hydrogen migration (**TS-7** for hydrogen 1,5-shift in 1,5-dichlorocyclopentadiene (**7**), **TS-8** for hydrogen 1,7-shift in 1,7-dichlorocycloheptatriene (**8**), and **TS-9** for chlorine 1,7-shift in 7-chlorocycloheptatriene (**9**). Atomic distances are in angstroms and angles in degrees. Energies at Becke3LYP/6-311G** are in kJ/mol. The values in italics are the charges calculated by Merz−Singh−Kollman scheme. Each value in parentheses is single imaginary frequency.

the two reactive terminals close to each other. Thus, the calculated $\Delta E^{\ddagger}$ values shown in Figures 3−5 are consistent with the rule that (hydrogen and chlorine) 1,5-sigmatropic shift proceeds relatively easily under the orbitally controlled suprafacial mode. The reactions are experimentally observed at 200−400 °C ($\Delta E^{\ddagger}$ values are estimated in the range 100−160 kJ/mol).[1e,1i]

Table 3 collects energetic parameters ($\Delta E^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$, and ΔZPE) for all the TSs discussed above. The tendency of the variations in activation energies ($\Delta E^{\ddagger}$), in free energies of activation ($\Delta G^{\ddagger}$), and in $\Delta E^{\ddagger}$s corrected by zero-point energy (ZPE) are fundamentally the same. Moreover, the calculations including diffusion function (Becke3LYP/6-311+G**) show fundamentally the same results as those with the values calculated at Becke3LYP/6-311G**. The larger changes of entropies at **TS-5** and **TS-6** are clearly attributed to the cyclic transition states from the chain structures of **5** and **6**.

As shown in Figure 6, the $\Delta E^{\ddagger}$ value (+297.2 kJ/mol) calculated at Becke3LYP/6-311G** for the hydrogen 1,5-shift (**TS-8**) in 1,7-dichlorocycloheptatriene (**8**) is close to that for **TS-2** (+288.0). The equality of these $\Delta E^{\ddagger}$s clarified that the substitution of hydrogen at 7-position by a chlorine atom hardly changes the $\Delta E^{\neq}$ value for hydrogen shift. This result adds evidence to support the interpretation that the remarkable difference in $\Delta E^{\ddagger}$s between **TS-8** and **TS-1** (from +297.2 kJ/mol for **TS-8** to +50.1 for **TS-1**) is due to the stabilization of **TS-1** by Coulomb interaction between the migrating anionic chlorine atom and cationic tropylium like fragment. The $\Delta E^{\ddagger}$ value (+37.9 kJ/mol) for **TS-9** for chlorine 1,7-shift in 7-chlorocycloheptatriene (**9**) is smaller than that (+50.1) for **TS-1**. The comparison of the energetics between **TS-1** and **TS-9** indicates that disubstitution by chlorine atoms at C1 and C7 in **TS-1** raises the activation energy for the 1,7-shift, which is consistent with the electron-withdrawing nature of the chlorine atom. The difference between $\Delta E^{\ddagger}$ values for **TS-7** (+142.5 kJ/mol) and **TS-4** (+116.2) in hydrogen 1,5-shift indicates that the disubstitution at C1 and C5 by two chlorine atoms in **7** also increases the activation energy for 1,5-shift. Thus, extra substitution by halogen atoms at C1 and C5 for 1,5-shift or at C1 and C7 for 1,7-shift makes $\Delta E^{\ddagger}$ a little larger. That is, extra chlorine substitution works as a repressing factor both for 1,5- or 1,7-sigmatropic shifts. Judging from these results, extra substitution by chlorine atoms at five- and seven-membered rings appears to make the reactivity both for 1,5- or 1,7-migration smaller, regardless of the nature of whether the rings tend to carry positive or negative charge. The effect of Coulomb interaction to promote 1,5-migration might be smaller as compared with the case in 1,7-shift. The charge growing on the migrating atom in 1,5-shift is generally smaller than that in 1,7-shift at transition state. This result is clearly attibuting to the difference between the negatively charged nature of the cyclopentadiene ring in 1,5-shift and positively charged nature of the tropylium ring in 1,7-shift in **1**.

The molecular orbital coefficients ($|\mathrm{Cl}^{m}{}_{\mathrm{HOMO}}|^2$ and $|\mathrm{Cl}^{m}{}_{\mathrm{LUMO}}|^2$) on migrating th chlorine atom were calculated to be 0.82 and 0.04 for **TS-1**, supporting the considerable charge separation between the anionic migrating chlorine atom and the cationic tropylium ring (shown in Table 2). For **TS-3**, the values of $|\mathrm{Cl}^{m}{}_{\mathrm{HOMO}}|^2$ and $|\mathrm{Cl}^{m}{}_{\mathrm{LUMO}}|^2$ are 0.19 and 0.49, implying that migrating chlorine has an electrophilic nature, and these coefficients are the reverse of those in **TS-1** and are consistent with the results that the seven-membered ring (**TS-1**) is cationic and the five-membered ring anionic (**TS-3**). Finally, for **TS-5** for a 1,5-shift in chainlike **5** the difference between the two coefficients on the migrating chlorine is the smallest (0.42 and 0.30), implying the smallest contribution of Coulomb interaction to the stabilization of the TS among these three cases. Thus, Coulomb interaction appears to vary its importance in the order **TS-1** ≫ **TS-3** > **TS-5**. In other words, the contribution of orbital interaction (the conservation of orbital symmetry) to the stabilization of TS becomes more important in the order **TS-5** > **TS-3** ≫ **TS-1**.

Summary

Theoretical study was performed on chlorine 1,7-shift and/or 1,5-shift in 1,7,7-trichlorocycloheptatriene (**1**), 1,5,5-trichlorocyclopentadiene (**3**), and 1,2,5-trichloro-1,3-pentadiene (**5**) by the analysis of transition state parameters obtained on the basis of density functional theory (DFT) at Becke3LYP/6-311G** level and Becke3LYP/6-311+G** level calculations. The calculations on 1,7-shift and/or 1,5-shift were also carried out on cycloheptatriene (**2**), cyclopentadiene (**4**), and 1,3-pentadiene (**6**) for comparison. The calculation at the Becke3LYP/6-311+G** level gave no significant difference compared to that at the Bekce3LYP/6-311G** level. The study revealed that the pathway of thermal intramolecular chlorine shift in **1** is 1,7-shift rather than 1,5-shift. The mechanism of the 1,7-shift is a concerted suprafacial shift through zwitterionic transition structure. With the assistance of Coulomb interaction between negatively charged chlorine atom and positively charged tropylium ring, the 1,7-shift mechanism energetically overwhelms the orbital symmetrically allowed 1,5-shift mechanism. Population analysis of the migrating chlorine atom (Cl^m) and tropylium ring gives the charges of −0.53 and +0.47 (Merz−Singh−Kollman scheme), respectively. This fairly large charge separation plays a significant role in stabilizing the transition state in thermal suprafacial chlorine 1,7-shift in **1**. The calculation shows that chlorine 1,7-shifts in **1** and 7-chlorocycloheptatriene (**TS-1** and **TS-9**, respectively) are good illustrations of suprafacial 1,7-shift and the orbitally allowed chlorine 1,5-shift in **1** (**TS-1′**) is more energetically unfavorable than **TS-1**. On the other hand, the difficulty of hydrogen 1,7-shift (**TS-2** and **TS-8**) and the ease of the chlorine 1,5-shift (**TS-3**, **TS-5**, and **TS-7**) and hydrogen 1,5-shift (**TS-2′**, **TS-4** and **TS-6**) are consistent with the prediction of W-H rule.

Supporting Information Available: Cartesian (XYZ) coordinates with total energies calculated at Becke3LYP/6-311G** and Becke3LYP/6-311+G** levels for all transition structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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