J. Org. Chem. **2002,** *67,* 1953−1960 **1953**

Gas-Phase Identity Nucleophilic Substitution Reactions of Cyclopropenyl Halides

Chang Kon Kim, Hong Guang Li, Bon-Su Lee, Chan Kyung Kim, Hai Whang Lee, and Ikchoon Lee*

Department of Chemistry, Inha University, Inchon 402-751, Korea

ilee@inha.ac.kr

Received December 24, 2001

The gas-phase identity nucleophilic substitution reactions of halide anions (X = F, Cl, and Br) with cyclopropenyl halides, $X^- + (CH)_3X \rightleftharpoons X(CH)_3 + X^-$, are investigated theoretically at four levels of theory, B3LYP/6-311+G**, MP2/6-311+G**, G2(+)MP2//MP2/6-311+G**, and G2(+)//MP2/6-311+G**. Four types of reaction paths, the σ-attack S_N2, π-attack S_N2'-syn, and S_N2'-anti and sigmatropic 1,2-shift, are possible for all the halides. In the fluoride anion reactions, two types of stable adducts, *syn*- and *anti*-1,2-difluorocyclopropyl anions, can exist on the triple-well-type potential energy surface of the identity substitution reactions with rearrangement of double bond (C═C), S_N2'-syn, and S_N2'-anti processes. The TSs for the σ-attack S_N2 paths have "open" (loose) structures so that the ring positive charges are high rendering strong aromatic *cyclopropenyl* (*delocalized*) *cation-like* character. In contrast, in the π-attack S_N2' paths, a lone pair is formed at the unsubstituted carbon (C3), which stabilizes the *1,2-dihalocyclopropyl* (*delocalized*) *anion-like* TS by two strong $n_C-\sigma^*_{C-F}$ vicinal charge-transfer delocalization interactions. The barrier height increases in the order S_N2'-anti < σ-attack S_N2 < S_N2'-syn for X = Cl and Br, whereas for X = F the order is changed to S_N2'-anti < S_N2'-syn < σ-attack S_N2 due to the stable difluoro adduct formation. The sigmatropic 1,2-shift (circumambulatory) reactions have high activation barriers and cannot interfere with the substitution reactions.

Introduction

Bimolecular nucleophilic substitution (S_N2) reactions at carbon are among the most extensively studied reactions of organic chemistry. The studies of S_N2 reactions in the gas phase have been particularly valuable as they allow investigations of various intrinsic molecular reactivity factors without involvement of solvent.

Early theoretical [1] as well as experimental [2] studies have established a double-well potential energy surface for the gas-phase S_N2 reactions. The most thoroughly studied reactions are the identity methyl transfer reactions involving halide anions, R = CH_3 with X = F, Cl, Br, and I in eq 1, especially with X = Cl.[1−3] Ab initio molecular orbital calculations have also been extended to the gas-phase identity S_N2 reactions at various primary and secondary carbons,[3a,4] and at various acyl functional centers.[5]

$$X^- + RX \rightarrow XR + X^- \qquad (1)$$

In this work, we have examined the set of identity halide-exchange reactions (eq 1) at a cyclopropenyl carbon, R = $(CH)_3$ with X = F, Cl, and Br, using up to G2(+) level of theory.[6] Nucleophilic substitution reactions of halide anions with cyclopropenyl halides are of much potential interests in view of the fact that (i) the displacement can occur by a σ- as well as π-attack (Scheme 1) and (ii) the cyclopropenyl cation and anion that may be involved in the reaction path are the simplest aromatic and antiaromatic species,[7] respectively.

Here, we report a systematic computational study of the reactions of F^- with cyclopropenyl fluoride (**1**), Cl^-

---

* To whom correspondence should be addressed. Fax: +82-32-8654855.

(1) (a) Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry. The S_N2 Mechanisms*; Wiley: New York, 1992. (b) Shi, Z.; Boyd, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 6789. (c) Vetter, R.; Zülicke, L. *J. Am. Chem. Soc.* **1990**, *112*, 5136. (d) Tucker, S. C.; Truhlar, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 3338. (e) Cho, Y. J.; Vande Linde, S. R.; Zhu, L.; Hase, W. L. *J. Chem. Phys.* **1992**, *96*, 8275. (f) Wang, H.; Peslherbe, G. H.; Hase, W. L. *J. Am. Chem. Soc.* **1994**, *116*, 9644. (g) Wladkowski, B. D.; Allen, W. D.; Brauman, J. I. *J. Phys. Chem.* **1994**, *98*, 13532. (h) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1995**, *117*, 2024.

(2) (a) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672. (b) Depuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 6850. (c) Van Doren, J. M.; Depuy, C. H.; Bierbaum, V. M. *J. Phys. Chem.* **1989**, *93*, 1130. (d) Wladkowski, B. D.; Brauman, J. I. *J. Phys. Chem.* **1993**, *97*, 13158. (e) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. (f) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993.

(3) (a) Lee, I.; Kim, C. K.; Chung, D. S.; Lee, B.-S. *J. Org. Chem.* **1994**, *59*, 4490. (b) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1995**, *117*, 2024. (c) Uggerud, E. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1459. (d) Botschwina, P. *Theor. Chem. Acc.* **1998**, *99*, 426. (e) Parthiban, S.; de Oliveira, G.; Martin, J. M. L. *J. Phys. Chem. A* **2001**, *105*, 895. (f) Hernandez, M. I.; Campos-Martinez, J.; Villarreal, P.; Shmatz, S.; Clary, D. C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1197. (g) Tonner, D. S.; McMahon, T. B. *J. Am. Chem. Soc.* **2000**, *122*, 8783.

(4) (a) Lee, I. *Chem. Soc. Rev.* **1995**, *24*, 223. (b) Lee, I.; Lee, H. W. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1529.

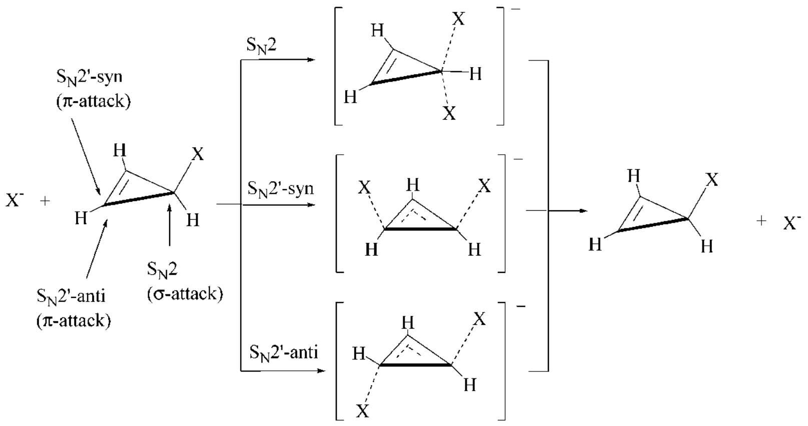
(5) (a) Kim, C. K.; Li, H. G.; Lee, H. W.; Sohn, C. K.; Chun, Y. I.; Lee, I. *J. Phys. Chem. A* **2000**, *104*, 4069. (b) Kim, C. K.; Hyun, K. H.; Kim, C. K.; Lee, I. *J. Am. Chem. Soc.* **2000**, *122*, 2294. (c) Lee, I.; Kim, C. K.; Li, H. G.; Sohn, C. K.; Kim, C. K.; Lee, H. W.; Lee, B.-S. *J. Am. Chem. Soc.* **2000**, *122*, 11162. (d) Sohn, C. K.; Ma, E. K.; Kim, C. K.; Lee, H. W.; Lee, I. *New J. Chem.* **2001**, *25*, 859.

(6) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(7) (a) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B, Ya. *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*; Wiley: New York, 1994. (b) Garrat, P. *Aromaticity*; Wiley: New York, 1986. (c) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393. (d) Glukhovtsev, M. N.; Laiter, S.; Pross, A. *J. Phys. Chem.* **1996**, *100*, 17801. (e) Byun, Y.-G.; Saebo, S.; Pittman, C. U. Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3689. (f) Merill, G. N.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 12322.

10.1021/jo0164047 CCC: $22.00

Scheme 1. Various Reaction Paths



X = F, Cl and Br

with cyclopropenyl chloride (**2**), and Br^- with cyclopropenyl bromide (**3**) (Scheme 1), together with the results of the corresponding S_N2 reactions of halide anions with the saturated compounds, cyclopropyl halides, and 1,2-sigmatropic halide shifts at the B3LYP/6-311+G**, MP2/6-311+G**, G2(+)MP2, and G2(+) levels of theory with the MP2/6-311+G** geometries.[8]

Computational Methods

Standard ab initio molecular orbital calculations were performed at the B3LYP/6-311+G**, MP2/6-311+G**, G2(+)-MP2//MP2/6-311+G**, and G2(+)//MP2/6-311+G** levels of theory[8] with the Gaussian98 system of programs.[9] All stationary points were confirmed with analytical second derivatives. Enthalpies ($\Delta H^{\ddagger}$) and free energies ($\Delta G^{\ddagger}$) of activation at 298 K were calculated using vibrational contributions obtained with the use of harmonic frequencies computed at the B3LYP/6-311+G** and MP2/6-311+G** levels and scaled by the appropriate factors.[10] All activation parameters reported are relative to the separated reactants level. The natural bond orbital (NBO) analyses [11] were carried out to determine the proximate charge-transfer energies in the transition states (TSs), and natural population analyses (NPA)[11] were performed. The percentage changes of bond order (%$\Delta n^{\ddagger}$)[12] upon TS formation were determined with eq 2

$$\%\Delta n^{\ddagger} = \frac{[\exp(-r^{\ddagger}/a) - \exp(-r_R/a)]}{[\exp(-r_P/a) - \exp(-r_R/a)]} \times 100 \qquad (2)$$

where $r^{\ddagger}$, r_R, and r_P are the bond length in the TS, reactant, and product, respectively, and a was set to 0.6 for bond order less than one and to 0.3 for bond order greater than 1.[12a]

Results and Discussion

I. Reactants and Reactant Complexes (RC). All the reactants, **1**–**3**, have C_s symmetry in which the symmetry plane bisects the molecular plane passing through C1 and the midpoint of the C=C bond. The double bond is slightly longer in **1** (1.320 Å) than those in **2** and **3** (1.315 Å). The isosceles single bonds are, however, shorter in **1** (1.470 Å) than in **2** and **3** (1.481 Å). As in other gas-phase identity nucleophilic substitution reactions of halide anions with alkyl halides, there are two identical ion–dipole complexes (reactant complexes) on either side of the central reaction barrier with a well-known double-well potential energy profile in all the reaction paths except for the π-attack S_N2' paths with X = F. In the latter reactions, stable adducts of C_S (S_N2'-syn) and C_2 (S_N2'-anti) symmetry are formed presenting triple-well energy profiles for the two reaction paths. We found two types of reactant complexes (RCs) depending on the reaction path followed, one for the σ-attack S_N2 path and the other for the π-attack S_N2' path. The global minima were, however, the complexes on the S_N2' path. The well depths at the MP2/6-311+G** level, $\Delta E_{RC} = E_{RC} - E_{react}$, were −14.0, −10.2, and −10.3 kcal mol^{-1} for the S_N2 path with X = F, Cl, and Br, respectively, and −14.0 and −12.8 kcal mol^{-1} for the S_N2' path with X = Cl and Br, respectively. In the S_N2' path, the reactant complex with X = F was evasive and was unobtainable due to deprotonation at the MP2/6-311+G** level. The complex was, however, located at the B3LYP/6-311+G** level, and the structures of all the complexes are presented in **S1** (Supporting Information).

II-1. $(CH)_3F + F^-$ Reaction. Cyclopropene having a double bond is known to be stabilized by fluorine substitution, as is found with 3,3-difluorocyclopropene.[13] The fluorine acts as an electron acceptor and reduces the electron density associated with the C=C bond, leading to an aromatic cyclopropenyl cation-like structure.[13] In the reaction of fluoride anion with cyclopropenyl fluoride (**1**), however, a loose weakly bonded adduct, 1,2-difluorocyclopropyl anion, is formed in the reactions with rearrangement of the double bond, S_N2'-syn and S_N2'-

---

[8] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, 1996.

[9] 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 98, Revision A.6;* Gaussian, Inc.: Pittsburgh, PA, 1998.

[10] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

[11] (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593. (c) Glendening, E. D.; Badenhoop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628.

[12] (a) Houk, K. N.; Gustabson, S. M.; Black, K. *J. Am. Chem. Soc.* **1992**, *114*, 8565. (b) Lee, I.; Kim, C. K.; Lee, B.-S. *J. Comput. Chem.* **1995**, *16*, 1045. (c) Lee, J. K.; Kim, C. K.; Lee, I. *J. Phys. Chem. A* **1997**, *101*, 2893.

[13] Wiberg, K. B.; Marquez, M. *J. Am. Chem. Soc.* **1998**, *120*, 2932.

Table 1. Energetics[a] for the Identity Reactions of Halide Anions with Cyclopropenyl Halides, at the G2(+)MP2//MP2/6-311+G Level (in kcal mol^{-1})**

X	path	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}_{\mathrm{ZPE}}$ [b]	$\Delta H^{\ddagger}$ [b]	$-\mathrm{T}\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$ [b]
F	S_N2	9.30	8.13	8.03	7.09	15.12
	(s-S_N2(back))[c]	(8.96)	(8.47)	(7.74)	(8.71)	(16.45)
	(s-S_N2(fro))[d]	(43.57)	(41.97)	(41.33)	(8.03)	(49.36)
	S_N2'-syn (TS)	−7.89	−7.88	−8.60	7.93	−0.68
	S_N2'-syn(int)	−12.98	−12.46	−13.15	8.17	−4.98
	S_N2'-anti(TS)	−12.95	−13.05	−13.78	8.05	−5.73
	S_N2'-anti(int)	−13.52	−13.64	−13.96	7.73	−6.23
Cl	S_N2	4.02	3.18	3.37	5.92	9.29
	(s-S_N2(back))[c]	(16.62)	(15.86)	(15.41)	(8.18)	(23.58)
	(s-S_N2(fro))[d]	(50.80)	(49.44)	(49.02)	(7.61)	(56.63)
	S_N2'-syn	6.43	6.24	5.62	7.99	13.61
	S_N2'-anti	−0.17	−0.43	−0.85	7.77	6.92
Br	S_N2	1.90	1.19	1.45	5.55	6.99
	(s-S_N2(back))[c]	(16.14)	(15.19)	(14.87)	(7.98)	(22.84)
	(s-S_N2(fro))[d]	(47.82)	(46.49)	(46.20)	(7.47)	(53.66)
	S_N2'-syn	6.33	6.13	5.58	7.90	13.48
	S_N2'-anti	−1.65	−1.96	−2.23	7.34	5.11

[a] The MP2/6-311+G** geometries were used. Thermal data were calculated at the MP2/6-311+G** level, and zero-point vibrational energies were corrected with the scaling factor of 0.9748. [b] At 298 K. [c] Backside attack for the saturated reactant (i.e., for cyclopropyl halides). [d] Frontside attack for the saturated reactant.

anti in Scheme 1. Thus, the reaction profiles for the π-attack S_N2'-paths are triple-well types, while the σ-attack ordinary S_N2 path has a double-well potential energy surface. Reference to the energetics summarized in Tables 1 and 2 reveals that the adducts formed are of extremely low stability, the well depth of the syn adduct ($\Delta E° = E_{\mathrm{adduct}} - E_{\mathrm{TS}} = -4.2$ kcal mol^{-1}) being deeper than that of the anti adduct ($\Delta E° = -0.1$ kcal mol^{-1} at the G2(+) level). The latter is so shallow that an inversion to $\Delta H° = H_{\mathrm{adduct}} - H_{\mathrm{TS}} = +0.3$ kcal mol^{-1} occurs with absurd results of the higher adduct level than the TS level when the thermal energy corrections are applied to the electronic energy.[5a,14] This type of inversion of stationary point levels in a flat transition structure region with an extremely shallow well is possible due to the loss of a vibrational degree of freedom in the TS (3N − 7) to an imaginary vibration.[5a,14] One less vibrational degree of freedom in the thermal energy component in the TS lowers the TS level below that of an adduct which has normal 3N − 6 degrees of vibrational modes. The relative energy levels become restored to normal only when the entropy effect is accounted for.[5a,14] The lower vibrational energy in the TS due to one less vibrational mode leads to a larger positive $-T\Delta S$ term (due to a larger negative ΔS value) and results in the higher G_{TS} than G_{adduct} level, $\Delta G° = G_{\mathrm{adduct}} - G_{\mathrm{TS}} = -0.1$ kcal mol^{-1}. It is to be noted that although the well depth in the S_N2'-syn path is deeper by 3.3 kcal mol^{-1}, the stability of the adduct is greater for the S_N2'-anti than S_N2'-syn (−5.7 vs −4.1 kcal mol^{-1}).

The energy barriers for all types of reaction including those for the fluoride exchanges in the cyclopropyl fluoride (s-S_N2(back) and s-S_N2(fro)) are underestimated at the B3LYP/6-311+G** level (**S2**, Supporting Information) due to overestimation of electron correlation effects for the TS. In contrast, they are overestimated at the MP2/6-311+G** level (**S3**, Supporting Information) relative to the higher level results at the G2(+) level (Table 2) due to underestimation of electron correlation effects for the TS. There are very small, insignificant, energy changes from G2(+)MP2 to G2(+) level.

Table 2. Energetics[a] for the Identity Reactions of Halide Anions with Cyclopropenyl Halides, at the G2(+)//MP2/6-311+G Level (in kcal mol^{-1})**

X	path	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}_{\mathrm{ZPE}}$ [b]	$\Delta H^{\ddagger}$ [b]	$-T\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$ [b]
F	S_N2	8.43	7.27	7.16	7.09	14.25
	(s-S_N2(back))[c]	(8.83)	(8.34)	(7.61)	(8.71)	(16.32)
	(s-S_N2(fro))[d]	(43.46)	(41.86)	(41.22)	(8.03)	49.24)
	S_N2'-syn (TS)	−7.91	−7.91	−8.63	7.93	−0.70
	S_N2'-syn(int)	−12.07	−11.55	−12.24	8.17	−4.07
	S_N2'-anti(TS)	−12.81	−12.91	−13.64	8.05	−5.59
	S_N2'-anti(int)	−12.95	−13.07	−13.39	7.73	−5.67
Cl	S_N2	3.85	3.01	3.20	5.92	9.11
	(s-S_N2(back))[c]	(17.05)	(16.29)	(15.83)	(8.18)	(24.00)
	(s-S_N2(fro))[d]	(51.41)	(50.05)	(49.64)	(7.61)	(57.25)
	S_N2'-syn	7.00	6.80	6.19	7.99	14.17
	S_N2'-anti	0.20	−0.06	−0.48	7.77	7.29
Br	S_N2	1.28	0.58	0.83	5.55	6.37
	(s-S_N2(back))[c]	(15.79)	(14.84)	(14.52)	(7.98)	(22.50)
	(s-S_N2(fro))[d]	(47.55)	(46.22)	(45.93)	(7.47)	(53.39)
	S_N2'-syn	6.43	6.24	5.69	7.90	13.59
	S_N2'-anti	−1.93	−2.23	−2.50	7.34	4.83

[a] The MP2/6-311+G** geometries were used. Thermal data were calculated at the MP2/6-311+G** level and zero-point vibrational energies were corrected with the scaling factor of 0.9748. [b] At 298 K. [c] Backside attack for the saturated reactant (i.e., for cyclopropyl halides). [d] Frontside attack for the saturated reactant.

The following discussion will be based on the G2(+) results. We note that barrier height for the direct σ-attack S_N2 reaction ($\Delta G^{\ddagger} = 14.3$ kcal mol^{-1}) is lower only by ca. 2 kcal mol^{-1} than that for the backside attack of F^- on the saturated reactant of cyclopropyl fluoride (16.3 kcal mol^{-1}). This is reasonable since in the σ-attack TS there is very small degree of rearrangement in the cyclopropenyl ring and the TS has a distorted trigonal bipyramidal pentacoordinate (TBP-5C) structure where the cyclopropenyl ring provides two equatorial ligands, Figure 1. The C_{2v} symmetry TS is quite similar to that of the backside attack on the cyclopropyl fluoride with a relatively open (loose) structure; the percentage bond order changes in the TS are ca. 33% bond formation and 67% bond cleavage (**S4**, Supporting Information). There are relatively small ring atom (C1−C3) charge shifts in the TS formation in both of the σ-attack processes (**S5**, Supporting Information). Due to the open structure of the TS with **1**, the ring (positive) charge increases by Δq

---

[14] Lee, I.; Kim, C. K.; Li, H. G.; Lee, B.-S.; Lee, H. W. *Chem. Phys. Lett.* **2000**, *320*, 307.

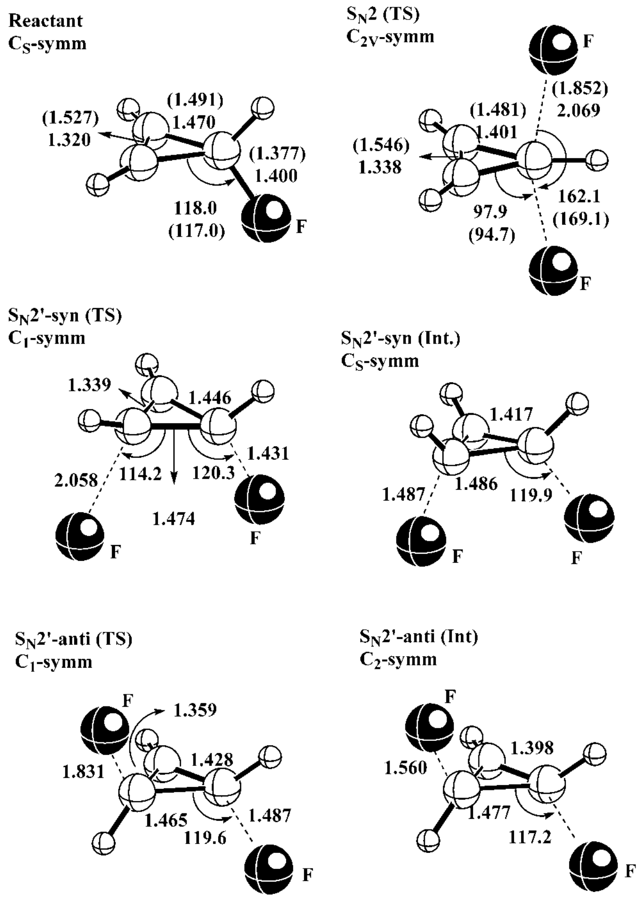


Figure 1. Structures of reactant and transition states for the identity reactions of cyclopropenyl fluoride, calculated at the MP2/6-311+G** level.

Scheme 2. 1,1-Dihalocyclopropenyl Cation-like TS Structure for the σ-Attack S$_N$2 Processes (X = F)

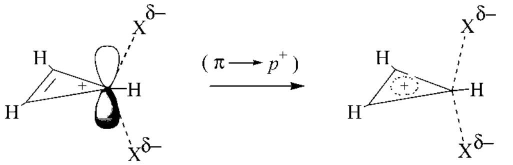


Table 3. Electrostatic (ΔE_{es}), Deformation (ΔE_{def}), and Charge-Transfer Energies ($\Sigma\Delta E^{(2)}_{\sigma-\sigma^*}$) for the Reactions of Cyclopropenyl Halides at the MP2/6-311+G Level (in kcal mol^{-1})**

X	path	ΔE_{es}[b]	ΔE_{def}	$-\Sigma\Delta E^{(2)}_{\sigma-\sigma^*}$[c]
F	S$_N$2	−61	46	307
	(s-S$_N$2(back))[a]	(−12)	(52)	139
	S$_N$2′-syn (TS)	22	4	79
	S$_N$2′-syn (int)	53	27	99
	S$_N$2′-anti (TS)	20	10	191
	S$_N$2′-anti (int)	34	23	156
Cl	S$_N$2	−87	41	352
	(s-S$_N$2(back))[a]	(−2)	(53)	120
	S$_N$2′-syn	42	25	270
	S$_N$2′-anti	16	26	345
Br	S$_N$2	−86	35	367
	(s-S$_N$2(back))[a]	(3)	(49)	117
	S$_N$2′-syn	37	24	377
	S$_N$2′-anti	−3	25	564

[a] Backside attack for the saturated reactants (i.e., for cyclopropyl halides). [b] The ΔE_{es} values shown are the *differences* in the electrostatic energies between the TS and reactant. $\Delta E_{es} = E_{es}(TS) - E_{es}(reactant)$. [c] The values listed are the *differences* in the total charge-transfer energies between the TS and reactant.

= +0.261 electronic charge unit to q_{ring} = +0.666e. The charge loss to the departing F$^-$ from the ring leaves an empty *p* orbital at C1, and a strong charge transfer occurs from the $\pi_{C=C}$ orbital to this empty p (p$^+$) forming a delocalized cyclopropenyl cation structure, Scheme 2. This π−p$^+$ type charge-transfer energy is the major component of the proximate bond (σ)−antibond (σ*) charge-transfer stabilization energies ($\Sigma\Delta E^{(2)}_{\sigma-\sigma^*}$, eq 3)[11] in Table 3. The π−p$^+$ charge-transfer energy increases successively from −232 (F) to −350 (Cl) and to −378 kcal mol^{-1} (Br) as the ring positive charge increases from +0.666 (F) to +0.744 (Cl) and to +0.762 (Br).

In contrast, there is only a slight positive charge increase (Δq = +0.026) in the TS with cyclopropyl fluoride. Due to the open TS structures for the σ-attack S$_N$2 processes, there is a stabilizing electrostatic effect (ΔE_{es} < 0) with a large deformation energy [1a,15] (ΔE_{def} > 0), which is needed to form the TS structure from the reactant (Table 3). The frontside attack S$_N$2 reaction of cyclopropyl fluoride has a large activation barrier ($\Delta G^\ddagger$ = 49.2 kcal mol^{-1}) due to unfavorable orbital overlap in the frontside approach of the nucleophile.[16]

The substitution with rearrangement of the double bond can occur through π-attack either with the syn (S$_N$2′-syn) or anti (S$_N$2′-anti) orientation (Scheme 1), the S$_N$2′-anti process being favored over the S$_N$2′-syn path by ca. 5 kcal mol^{-1} (Table 2). The TS for the former (49% bond making with 14% bond cleavage) is somewhat later along the reaction coordinate than the latter path (33% bond making with 5% bond cleavage) (**S4**, Supporting Information), and the ring positive charge in the TS is greater with the S$_N$2′-syn (+0.260) rather than with the S$_N$2′-anti (+0.202) process (**S5**). The electrostatic (ΔE_{es}) and deformation energies (ΔE_{def}) for the two paths are similar. However, in the S$_N$2′-anti path the proximate charge-transfer stabilization energies,[11,17] $\Sigma\Delta E^{(2)}_{\sigma-\sigma^*}$ in eq 3

$$\Delta E^{(2)}_{\sigma-\sigma^*} = -\sum \frac{2F^{2}_{\sigma\sigma^*}}{\epsilon_{\sigma^*} - \epsilon_{\sigma}} \tag{3}$$

are much greater (−191 kcal mol^{-1}) than that for the S$_N$2′-syn path (−79 kcal mol^{-1}). The main contribution of the proximate charge-transfer delocalization energy in the S$_N$2′ processes comes from an interaction between the developing lone pair on C3 (n$_C$) and the two vicinal C−F antibonding (σ*) orbitals ($n_C-\sigma^*_{C-F}$ interactions). As the nucleophile approaches to the double bond at C2, the double bond is broken and the C3 carbon becomes pyramidalyzed (Scheme 3) forming a nonbonding orbital (n) and two strong vicinal $n_C-\sigma^*_{C-F}$ charge-transfer delocalization interactions can occur. For example, the NBO analyses [11] have shown that in the S$_N$2′-syn adduct (C_s symmetry) the lone pair level is 0.0371 au and the two

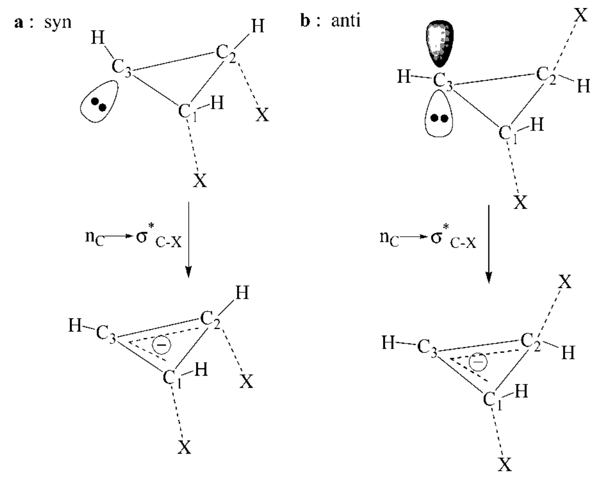
---

(15) Mitchell, D. J.; Schlegel, H. B.; Shaik, S. S.; Wolfe, S. *Can, J. Chem.* **1985**, *63*, 1642.

(16) Glukhovtsev, M. N.; Pross, A.; Schlegel, H. B.; Bach, R. D.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 11258.

(17) (a) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R.; Bernardi, F. *Structural Theory of Organic Chemistry*; Springer-Verlag: Berlin, 1977; Part IV. (b) Musso, G. F.; Figarri, G.; Magnasco, V. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1243.

Scheme 3. 1,2-Dihalocyclopropyl (Delocalized) Anion-like TS Structures for S_N2'-Processes ($X = F$)



σ^*_{C-F} levels are 0.5757 au, whereas in the S_N2'-anti adduct (C_2 symmetry) the corresponding levels are 0.0454 and 0.4998 au, respectively. This means that the energy gap $\Delta\epsilon = \epsilon_{\sigma^*} - \epsilon_n$ in eq 3 is ca. 0.54 and 0.45 au, respectively, so that S_N2'-anti has smaller energy gap by ca. 0.09 au leading to a larger vicinal $n_C-\sigma^*_{C-F}$ charge-transfer delocalization stabilization (eq 3) for the S_N2'-anti adduct. These energy level differences are caused by the structural difference in the two adducts; in the S_N2'-syn adduct all the hydrogen atoms are turned away from the ring plane upward in the opposite direction to the two relatively short C−F bonds (higher σ^* level) (Figure 1) so that the sp^3 type lone pair (lower level) on the C3 atom face downward, whereas in the S_N2'-anti adduct the lone pair is a p type (higher level) with the two relatively long C−F bonds (lower σ^* level). The greater vicinal $n_C-\sigma^*_{C-F}$ charge-transfer energies[11,17] in the S_N2'-anti TS leads to the more favored S_N2'-anti path by ca. 5 kcal mol^{-1} over the S_N2'-syn path.

The order of increasing *reactivity* predicted by the G2(+) theory is thus s-S_N2 ($\Delta G^\ddagger = 16.3$ kcal mol^{-1}) < S_N2 (14.3) < S_N2'-syn (−0.7) < S_N2'-anti (−5.6) for the identity nucleophilic substitution reactions of F^- with cyclopropenyl (**1**) and cyclopropyl fluoride.

II-2. $(CH)_3Cl + Cl^-$ Reaction. The chlorine does not form as stable an adduct as the 1,2-dichlorocyclopropyl anion so that all the reaction paths, S_N2, S_N2'-syn and S_N2'-anti, involving chloride exchanges in cyclopropenyl chloride (**2**) have double-well potential energy surfaces. Similar to the fluorine substitutions, all the activation energies (for S_N2, S_N2', and s-S_N2 processes) calculated at the B3LYP/6-311+G** level (**S2**) are lower (underestimated) than those at the G2(+) level (Table 2) due to overestimation of electron correlation effects for the TSs.

At the MP2 level, the electron correlation effects are known to be overestimated for the (electronic) charge delocalized system, whereas it is underestimated for the charge localized system.[18] We note that the activation energies ($\Delta E^\ddagger$ and $\Delta G^\ddagger$) for the σ-attack S_N2 processes are higher, whereas those are lower for the π-attack S_N2' paths with X = Cl and Br at the MP2 level (**S3**) than those corresponding values at the G2(+)level (Table 2).

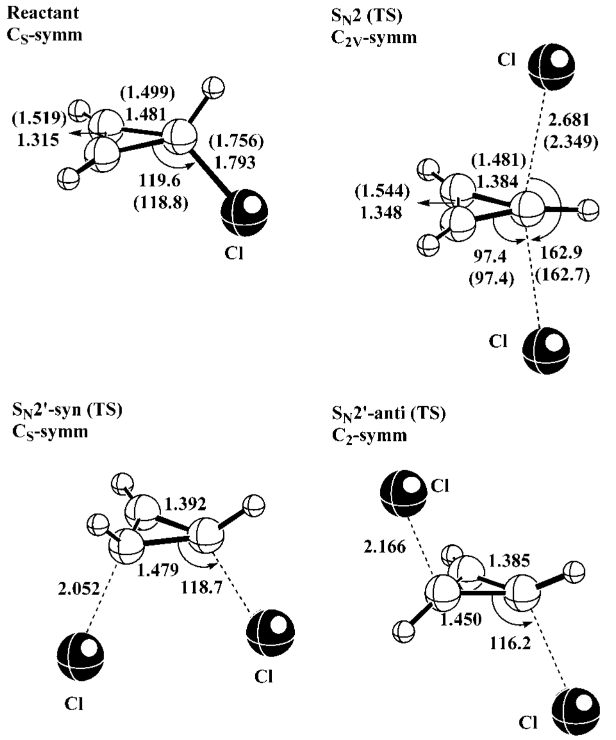


Figure 2. Structures of reactant and transition states for the identity reactions of cyclopropenyl chloride, calculated at the MP2/6-311+G** level.

This implies that the S_N2' TSs with X = Cl and Br have relatively larger (electronic) charge delocalization than the corresponding TSs with X = F. This is reasonable since the S_N2' TSs with X = Cl and Br have relatively larger degree of bond formation (46−65%) and bond cleavage (36−54%) leading to relatively stronger $n_C-\sigma^*_{C-X}$ vicinal charge-transfer stabilization within the cyclopropyl anion like TS structures (Scheme 3) than the TSs with X = F, which have lower degree of bond formation (33−49%) and bond cleavage (5−14%). It is to be noted that in general the stronger the vicinal bond(σ)−antibond(σ^*) interaction (in the present case, $n_C-\sigma^*_{C-X}$ interactions) the stronger the bond between the two interacting bond orbitals becomes[11] (in the present case, d_2(C1−C3) and d_3(C2−C3) bonds in Scheme 3). Thus, the stronger (electronic) charge delocalization of the lone pair on C3 (n_C) leads to larger double-bond character (or shorter bond lengths) for the d_2 and d$_3$ bonds with X = Cl ($d_2 = d_3 = 1.392$ (syn); 1.385 Å (anti)) and Br (1.390 (syn); 1.380 Å (anti)) than with X = F (1.417 (syn); 1.398 Å (anti)) (**S4**, Supporting Information). These comparisons clearly show that the TSs for the S_N2' paths with X = Cl and Br have stronger delocalized structures than with X = F.

The identity S_N2 reactions of cyclopropyl chloride (s-S_N2(back) and s-S_N2(fro)) have much higher reaction barriers ($\Delta G^\ddagger = 24.0$ and 57.3 kcal mol^{-1}) than those of cyclopropenyl chloride (**2**). In the σ-attack S_N2 TS for **2** there is a strong stabilizing positive charge development in the ring (+0.744). This is due to an open TS structure (Figure 2) with extended C−Cl bond length of 2.681 Å, which is longer than that in the s-S_N2(back) TS by 0.34 Å. The strong cationic charge of the cyclopropenyl ring affords aromatic (cyclopropenyl cation) ring structure (Scheme 2) and also relatively strong electrostatic sta-

---

(18) (a) Carsky, P.; Urban, M. *Ab Initio Calculations. Methods and Applications in Chemistry;* Springer-Verlag: Berlin, 1980; p 79. (b) Li, H. G.; Kim, C. K.; Lee, B.-S.; Kim, C, K.; Rhee, S. K.; Lee, I. *J. Am. Chem. Soc.* **2001**, *123*, 2326.

bilization ($\Delta E_{es} = -87$ kcal mol^{-1}) leading to the low reaction barrier ($\Delta G^{\ddagger} = 9.1$ kcal mol^{-1}).

The TS structures in Figure 2 reveal that the C−Cl bond length is substantially longer (by 0.114 Å) in the S_N2'-anti TS (C_2-symmetry) than that in the S_N2'-syn (C_s-symmetry). Actually, the S_N2'-anti TS (54% bond making and 46% bond cleavage) has a slightly looser structure with a lower degree of bond formation and a greater degree of bond cleavage than the S_N2'-syn TS (65% bond formation and 35% bond cleavage). Overall, the two TSs for the S_N2' processes have 1,2-dichlorocyclopropyl (delocalized) anion-like structures (Scheme 3). In addition to a greater steric and electrostatic repulsion between the two chlorine atoms in the syn TS ($\Delta E_{es} = +42$ kcal mol^{-1}) than in the anti TS (+16 kcal mol^{-1}), the proximate charge-transfer delocalization stabilization energies ($-\Sigma\Delta E^{(2)}_{\sigma-\sigma^*}$) are also lower for the syn (−270 kcal mol^{-1}) than for the anti TS (−345 kcal mol^{-1}). This smaller charge-transfer stabilization for the S_N2'-syn TS is due mainly to the two weaker $n_C-\sigma^*_{C-Cl}$ interactions in the syn than in the anti TS. Here again, as in the fluoride S_N2' processes (vide supra), the carbanionic center (C3) has pyramidalyzed sp^3 type lone pair (lower n level of 0.0314 au) in the S_N2'-syn TS, whereas it is a p type (higher n level of 0.0396 au) in the S_N2'-anti TS (Scheme 3 and Figure 2). Thus, the energy gap, $\Delta\epsilon = \epsilon_{\sigma^*} - \epsilon_n$, is greater for the S_N2'-syn TS ($\Delta\epsilon = 0.21$ au) than for the S_N2'-anti TS ($\Delta\epsilon = 0.13$ au), which of course leads to the lower degree of proximate charge-transfer delocalization for the syn TS. The activation barrier is considerably higher for the syn ($\Delta G^{\ddagger} = 14.2$ kcal mol^{-1}) than for the anti path ($\Delta G^{\ddagger} = 7.3$ kcal mol^{-1}). The order of increasing *reactivity* is thus s-S_N2(front) < s-S_N2(back) < S_N2'-syn < S_N2 < S_N2'-anti.

For the chloride exchanges, the σ-attack S_N2 path is favored over the π-attack S_N2'-syn process. This is in contrast to the fluoride exchanges where the π-attack S_N2'-syn path has been shown to be favored over the σ-attack S_N2 path (vide supra). The main reasons for this reversal in favor of the σ-attack S_N2 path over the π-attack S_N2'-syn path in the chloride exchanges are (i) strong stabilization due to strong cationic ring charge in the σ-attack S_N2 path (Scheme 2) with a very open TS structure in the chloride exchanges and (ii) the stronger repulsion between the two chlorine atoms than between the two F atoms in the S_N2'-syn TS with larger destabilizing ΔE_{es} and ΔE_{def} values (Table 3).

II-3. $(CH)_3Br + Br^-$ Reaction. The bromide exchange reaction is quite similar to the chloride exchange reaction. 1,2-Dibromocyclopropyl anion is also not stable enough to exist as an intermediate. The potential energy surface is thus a double-well type. The σ-attack S_N2 TS has “open” (loose) structure with 22% bond formation and 78% bond cleavage and large ring positive charge of +0.762. As a results the TS is stabilized by a substantial aromatic cyclopropenyl cation character (Scheme 2) as well as by a strong electrostatic stabilization energy ($\Delta E_{es} = -86$ kcal mol^{-1}). In contrast, the S_N2 reaction of the saturated analogue, cyclopropyl bromide, has large energy barrier, for backside (22.5 kcal mol^{-1}) and frontside attack (53.4 kcal mol^{-1}) processes, where no such stabilizing factors are present in the respective TSs.

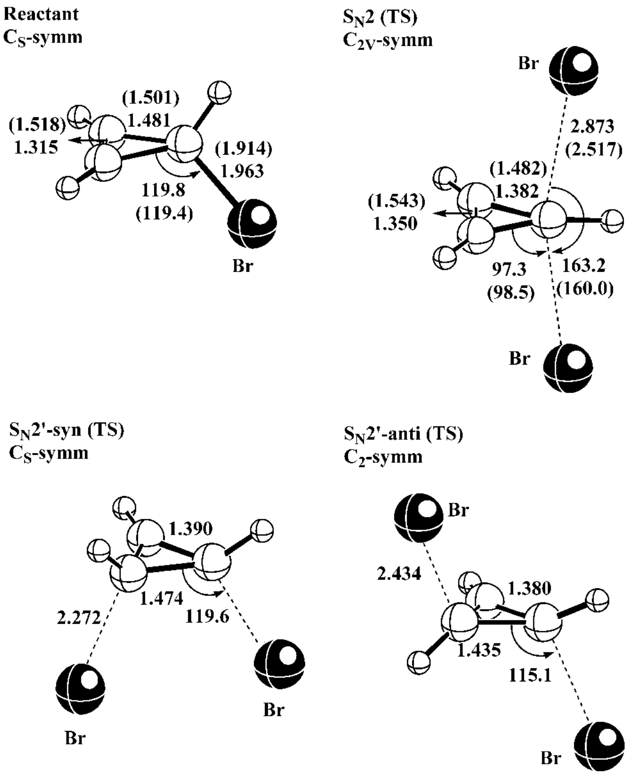
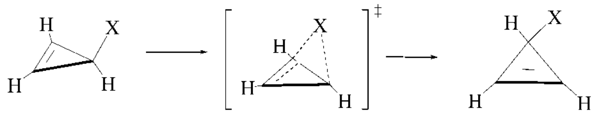


Figure 3. Structures of reactant and transition states for the identity reactions of cyclopropenyl bromide, calculated at the MP2/6-311+G** level.

Scheme 4. 1,2-Sigmatropic Rearrangements



X = H, F, Cl and Br

In the π-attack S_N2'-syn TS the ring positive charge (−0.108) is considerably lower than that in the S_N2'-anti TS (+ 0.244), and hence, the S_N2'-syn path is disfavored by the repulsive electrostatic interaction. The TS structures in Figure 3 show that the C−Br bond is much longer in the anti (C_2 symmetry) TS (2.434 Å) than in the syn (C_s symmetry) TS (2.272 Å). The lone pair in the latter ($\epsilon_n = 0.0282$ au) has a pyramidalyzed (sp^3) form, whereas that in the former is a p-type ($\epsilon_n = 0.0323$ au) in a 1,2-dibromocyclopropyl anion like TS (Scheme 3). The two σ^*_{C-Br} levels are $\epsilon_\sigma = 0.2335$ au for syn and $\epsilon_\sigma = 0.1581$ au for anti TS so that the energy gap in the former is wider by ca. 0.08 au than in the latter. Thus, the $n_C-\sigma^*_{C-Br}$ charge-transfer energy is much lower for the syn than anti leading to the total proximate charge-transfer delocalization energies of −377 kcal mol^{-1} (syn) and −564 kcal mol^{-1} (anti). The *reactivity* increases in the order s-S_N2(fro) < s-S_N2(back) < S_N2'-syn < S_N2 < S_N2'-anti. Here again, the π-attack S_N2'-syn path has a higher activation barrier than the σ-attack S_N2 path.

II-4. Sigmatropic 1,2-Shift (Circumambulatory Rearrangement). One specific type of pericyclic reaction is the so-called circumambulatory (merry-go-round) rearrangement [19] (Scheme 4). In this reaction, a migrant (X) displaces around the periphery of a conjugated ring during which the migrant becomes bonded to any of the

---

(19) (a) Childs, R. F. *Tetrahedron* **1982**, *38*, 567. (b) Minkin, V. I.; Minyaev, R. M.; Dorogan, I. V. *THEOCHEM* **1998**, *398*−*399*, 237. (c) Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988.

Table 4. Energetics[a] for Sigmatropic Rearrangements of Cyclopropenyl Halides, Calculated at the G2(+)MP2 and G2(+) Levels (in kcal mol^{-1})

method	X	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}_{\mathrm{ZPE}}$	$\Delta H^{\ddagger\,b}$	$-T\Delta S^{\ddagger b}$	$\Delta G^{\ddagger\,b}$
G2(+)MP2	H	93.57	88.89	88.87	−0.37	88.51
	F	45.24	43.60	43.72	−0.30	43.42
	Cl	33.65	32.47	32.58	−0.40	32.18
	Br	29.61	28.65	28.71	−0.38	28.33
G2(+)	H	93.56	88.87	88.85	−0.37	88.49
	F	44.91	43.27	43.39	−0.30	43.09
	Cl	33.55	32.37	32.48	−0.40	32.08
	Br	29.14	28.18	28.24	−0.38	27.86

[a] The MP2/6-311+G** geometries were used, and thermal data were taken from the same level. Zero-point vibrational energies were corrected with the factor of 0.9748. Bond energies of the C−H, C−F, C−Cl, and C−Br bonds are 107, 128, 96, and 84 kcal mol^{-1}, respectively.[20] [b] At 298 K.

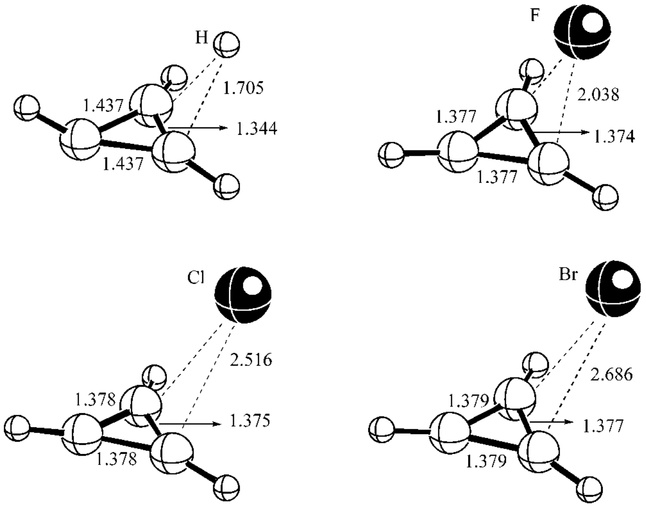
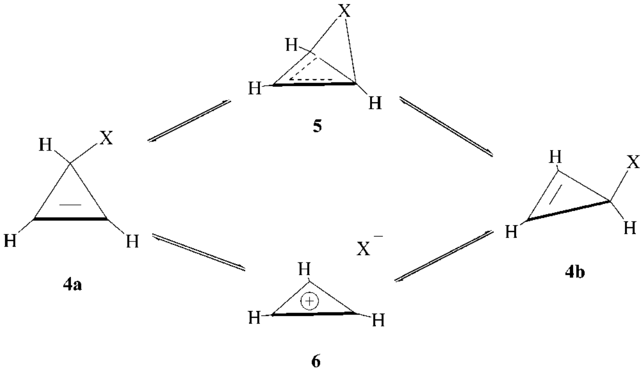


Figure 4. Structures of transition states for the sigmatropic rearrangement reactions of cyclopropenyl halides, calculated at the MP2/6-311+G** level (bond lengths in Å).

Scheme 5. Two Reaction Pathways for the 1,2-Sigmatropic Rearrangements



ring centers. In the cyclopropenyl halides this corresponds to a succession of 1,2-shifts. This reaction is formally a suprafacial 1,3-sigmatropic shift.[19] The barriers to the migration of X increases in the order X = Br < Cl < F < H (Table 4). Again, the activation barriers (**S6**, Supporting Information) are underestimated at the B3LYP/6-311+G** level and overestimated at the MP2/6-311+G** level relative to those corresponding values at the G2(+) level. For the migration of H, the $\Delta G^{\ddagger}$ = 88.5 kcal mol^{-1} at the G2(+) level is close to the bond energy [20] of the C−H bond (BE = 107 kcal mol^{-1}). The reaction with X = H is formally forbidden and there is no evidence for the degenerate rearrangement of cyclopropene itself.[21] Thermally induced rearrangements of this type have not been reported for simply substituted cyclopropenes. For the halogen atom migration the barriers are much less than their corresponding C−X bond energies (BEs) amounting slightly less than 1/2 of the BEs. This indicates that the energy needed for bond cleavage of C−X is compensated for by other TS stabilizing effect, especially in the migration of halogen atoms. The percentage bond order change (%$\Delta n^{\ddagger}$)indicate that the extent of bond cleavage increases from H (75%) to Br (86%) while the degree of bond making decreases from H (25%) to Br (15%) successively. The TS structures in Figure 4 show that the migrant (X) is farther away successively from X = H($d^{\ddagger}_{\mathrm{C-H}}$ = 1.705 Å) to X = Br ($d^{\ddagger}_{\mathrm{C-Br}}$ = 2.686 Å) with C_s symmetries. The ring charge in the TS for X = H is much smaller ($q_{\mathrm{ring}} = +0.133$) than those for X = F (+0.695), Cl (+0.662), and Br (+0.662), suggesting that due to the lower aromatic cyclopropenium cationic character with X = H the barrier to the migration of H almost corresponds to the C−H bond energy. The three C−C bond lengths within the ring (Figure 4) are nearly equal in the TS for X = F, Cl, and Br supporting the strong cyclopropenium cation character [22] exhibited by the strong ring positive charges.

Greater aromatic cylcopropenium cation character for the TSs with X = halogen reduces their barrier heights to ca. 1/2 of their corresponding C−X bond energies. The barriers to the 1,2-shifts are, however, considerably higher than those involved in the nucleophilic substitution reactions of halide anions with cyclopropenyl halides discussed above. We therefore conclude that the circumambulatory rearrangements of halides in cyclopropenyl halides will not interfere with the nucleophilic substitution reactions.

We have correlated the activation energies ($\Delta G^{\ddagger}$ at the G2(+) level) with bond energy (BE in kcal mol^{-1}) and electronegativity (χ) in eq 4. We note that $\Delta G^{\ddagger}$

$$\Delta G^{\neq} = (1.34 \pm 0.09)\mathrm{BE} - (41.38 \pm 2.36)\chi + (36.16 \pm 8.76)\ (r = 0.997) \quad (4)$$

increases with the BE of the C−X bond but decreases with the electronegativity (χ) of X, which is in agreement with the stability of the TS with a cyclopropenyl cation-like structure, **6** in Scheme 5.

Minkin et al.[19b] have shown that the circumambulatory rearrangements in cyclopropenyl halides can proceed via two reaction pathways, **4a** ⇌ **5** ⇌ **4b** and **4a** ⇌ **6** ⇌ **4b** in Scheme 5. The TS or intermediate structure **5** can be regarded as heterocyclic analogue of bicyclo[1.1.0] butyl cation. The other reaction path is associated with ionization of the cyclopropene and formation of an ion pair, **6**, whose subsequent random recombination leads to equilibration of a migrant X between all possible positions in the three-membered ring. Polar solvents favor the occurrence of the rearrangement through an ionization-recombination mechanism. Their results at the semiempirical MNDO/PM3 level,[19b] $\Delta E^{\ddagger}$ = 90.9 (F), 40.1 (Cl), and 24.3 kcal mol^{-1} (Br) differ substantially from our activation barriers at the G2(+) level, $\Delta E^{\ddagger}$ = 44.9 (F), 33.6 (Cl),

---

(20) The bond energies (BE) were calculated at the G2(+) level in terms of enthalpies.

(21) Sublett, B.; Bowman, N. S. *J. Org. Chem.* **1961**, *26*, 2594.

(22) Jursic, B. S. *THEOCHEM* **1999**, *491*, 193.

and 29.1 kcal mol^{-1} (Br). Comparison of the two sets of barrier heights indicates that the semiempirical method overestimates the barriers for X = F and Cl, whereas it underestimates the barrier for X = Br, so that there is no definite trend in the semiempirical activation energies with respect to the higher level correlated energies. The migration of X = Cl and Br corresponds almost to the ionization-recombination path, since bond cleavage is large (>85%) and the progress of bond formation is low (<15%) in the TS. Relatively low activation barriers for the migration of X = Cl and Br in Table 4 can be attributed to this strong aromatic cyclopropenium cation structure in the TS coupled with relatively low energy required to cleave the C−Cl and C−Br bonds.

III. Relative Reactivities. The activation energies for the σ-attack S_N2 processes decrease in the order F > Cl > Br, which is the sequence of increasing leaving ability and decreasing nucleophilicity. This is reflected in the extent of increasing bond cleavage (67% (F), 77% (Cl) and 78% (Br) and decreasing bond formation (33% (F), 23% (Cl) and 22% (Br)) in the TS. This means that the TS becomes successively more open (or loose) from X = F to Br resulting in an increasing aromatic cyclopropenium cation character due to the increase in the delocalized ring positive charge at the TS with +0.666 (F), +0.744 (Cl), and +0.762 (Br). The charge delocalization from the C═C bond toward the empty p orbital formed at C1 in the TS increases in the same order (Table 3). Thus, the reactivity order found for the σ-attack S_N2 processes can be explained by the increasing cyclopropenyl cation like aromatic character due to the decreasing nucleophilicity (F > Cl > Br) and increasing leaving ability of the halides (F < Cl < Br).

The activation energies of other processes, S_N2'-syn, S_N2'-anti, and the S_N2 reactions at the saturated analogues (i.e., cyclopropyl halides) all have the same trend of increasing order, F < Br < Cl. This is obviously at variance with that found for the σ-attack identity S_N2 reactions of cyclopropenyl halides discussed above, but is consistent with the reactivity order found for the identity methyl transfer reactions,[1c,h,3c,f,23] eq 1 with R = CH_3. For the identity methyl transfer reactions, the fact that the barrier height with X = F is the lowest (F < Br < Cl) has been predicted only when electron correlation effects are properly accounted for with relatively high level computation.[1c,h,3c,f,23] Lower level calculations predicted wrong barrier height orders, e.g., at the HF/4-31G level,[15] $\Delta E^{\ddagger} = 11.7$ and 5.5 kcal mol^{-1} for X = F and Cl, respectively, and at the MP4 level $\Delta E^{\ddagger} = 2.3$ and 1.8 kcal mol^{-1} for X = Br and Cl, respectively.[24] The low energy barrier for X = F has been attributed to an "open" TS structure in which a strong electrostatic stabilization with X = F lowers the reaction barrier sufficiently below that with X = Cl and Br.[5b]

This explanation for the lowest energy barrier with X = F seems to apply also for the identity halide exchanges in cyclopropyl halides (s-S_N2) processes, but not for the S_N2' processes.

As noted in II-1, the 1,2-difluoro anionic adducts in the S_N2'-syn and S_N2'-anti are stable enough to exist as intermediates in the triple-well potential energy surface. The stable 1,2-dihalo adducts formation is possible only with X = F, not with X = Cl and Br, in the S_N2' reaction paths. Although the 1,2-dihalocyclopropyl anion adduct (TS or intermediate) is stabilized mainly by the strong $n_C-\sigma^*_{C-F}$ interactions, the proximate charge-transfer delocalization ($\Delta E^{(2)}{}_{\sigma-\sigma^*}$ in Table 3) is not the only factor that is responsible for the stable adduct formation with X = F. This is because, the $\Sigma\Delta E^{(2)}{}_{\sigma-\sigma^*}$ value is actually the lowest with X = F (99 and 156 kcal mol^{-1} for S_N2'-syn(int) and S_N2'-anti(int), respectively) and the values are more negative and hence more stabilizing with X = Cl (270 and 345 kcal mol^{-1} for S_N2'-syn and S_N2'-anti TS, respectively) and X = Br (377 and 564 kcal mol^{-1} for S_N2'-syn and S_N2'-anti TS, respectively). This means that there are other factors that are contributing to the stable adduct formation with X = F. One such factor may be the bond energy (BE), since when an additional C−F bond is formed in the 1,2-adduct the bond energy gain is 128 kcal mol^{-1},[20] whereas in a C−Cl (BE = 96 kcal mol^{-1}) and C−Br (BE = 84 kcal mol^{-1}) bond formation much lower energy gain [20] is provided. The larger energy gain (greater than ca. 35 kcal mol^{-1}) with the C−F bond formation in the adduct in addition to the strong $n_C-\sigma^*_{C-F}$ charge-transfer stabilization seem to provide sufficient energy to form the stable adducts with X = F.

Summary and Conclusion

Four types of reaction paths, σ-attack S_N2, π-attack S_N2'-syn, and S_N2'-anti and 1,2-sigmatropic shift, are studied at four levels of theory, B3LYP/6-311+G**, MP2/6-311+G**, G2(+)MP2//MP2/6-311+G**, and G2(+)//MP2/6-311+G**, for the gas-phase identity halide anion reactions with cyclopropenyl halides $X^- + (CH)_3X \rightleftharpoons X(CH)_3 + X^-$ with X = F, Cl, and Br. For fluoride, stable adducts, 1,2-difluorocyclopropyl anion ($(CH)_3F_2^-$) with syn and anti orientations of the two F, can exist leading to a triple-well potential energy surface in the substitution reaction with rearrangement of double bond (C═C), S_N2'-syn and S_N2'-anti. In the σ-attack S_N2 reactions, the TSs are "open" or loose with high positive ring charge determining the barrier heights in the order Br < Cl < F. In the π-attack processes a lone pair is formed at C3 resulting in a cyclopropyl delocalized anion type TS. The anionic TSs in S_N2'-syn and S_N2'-anti processes are stabilized by the two strong vicinal charge-transfer interactions, $n_C-\sigma^*_{C-X}$. As a result, the activation barrier increases in the order S_N2'-anti < σ-attack S_N2 < S_N2'-syn for X = Cl and Br, whereas the order for X = F is S_N2'-anti < S_N2'-syn < σ-attack S_N2 due to the formation of stable difluorocycopropyl adducts. The sigmatropic 1,2-shift (circumambulatory) reactions have high activation barriers so that cannot interfere with the substitution reactions. In all the reactions involving π-attack the barrier height increases in the order F < Br < Cl.

Acknowledgment. This work was supported by the Korea Research Foundation (Grant No. KRF-2000-015-DP0208).

Supporting Information Available: Structures of reactant complexes, energetics at the B3LYP/6-311+G** and MP2/6-311+G** levels, percentage bond order changes, atomic charges, total energies, and all *Z*-matrixes at the MP2/6-311+G** level. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0164047

---

(23) Lee, I.; Kim, C. K.; Sohn, C. K.; Li, H. G.; Lee, H. W. *J. Phys. Chem. A.* **2002**, *106*, 1081.

(24) Deng, L.; Branchadell, V.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 10645.