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Zigzag Collapse of Four-Membered Rings Generated by Additions of Halonium Ions to Cyclopropanes

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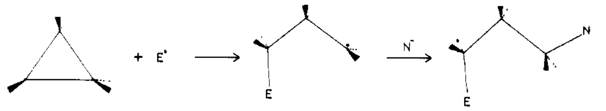
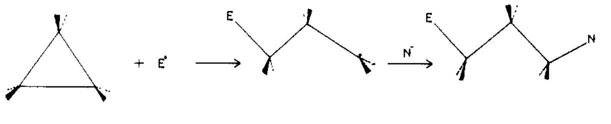
Contribution from the Educational Technology Center, Nara University of Education, Takabatake, Nara 630, Japan, Yuge Mercantile Marine College, Yuge, Ochi, Ehime 794-25, Japan, and Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11, Japan. *Received October 13, 1987. Revised Manuscript Received April 20, 1988*

Abstract: The ring-cleavage processes of cyclopropane by some electrophiles were studied with the aid of the ab initio MO calculations. For the electrophile E^+ without any lone pairs, e.g., H^+, the reactions generate an ethylene–methyl cation π-complex. The following attack by the nucleophile N^- occurs on the back side of the ethylene moiety, i.e., with inversion of configuration (N-inversion). The E-retention is preferential due to the properties of the π-complex. For E^+ with lone pairs, e.g., Cl^+ and Br^+, a four-membered ring species forms as a stable intermediate. The cyclic compound collapses in a zigzag manner via the transition state into the 3-halopropyl cation. The TS geometry is close to that of the ethylene–methyl cation π-complex. The zigzag collapse of the four-membered ring was found to be an elementary process in organic reactions. The stereochemical outcome is the double E,N-inversion. The stability of the four-membered species is discussed in terms of the symmetry property of the orbitals involved in cyclic interactions.

The present paper describes a theoretical study of electrophilic additions of cyclopropanes (CPs). The mechanism has been investigated both experimentally[1] and theoretically.[2] The ring opening yields two stereochemically different types of products:



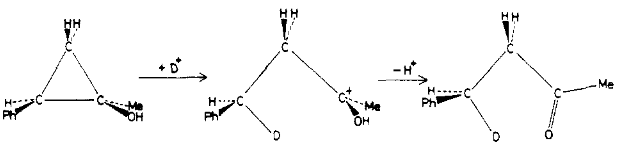
(1)



(2)

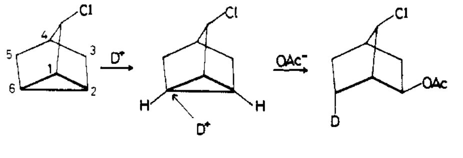
In eq 1, the stereochemical configuration is retained for the electrophile E^+ (E-retention) and inverted for nucleophile N^- (N-inversion). In eq 2, the configurations are inverted at both reaction centers (double E,N-inversion).

For example, the E-retention is exemplified by the following reaction (eq 1a):[3] The process of the E-retention and N-inversion



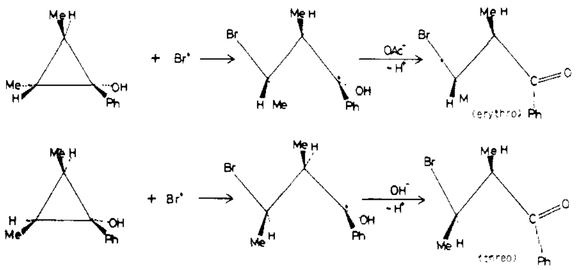
(1a)

has been observed for the reaction in D_2SO_4–DOAc (eq 1b).[4] The deuterium is incorporated in the endo direction at C_6 with the acetate group in the exo direction.



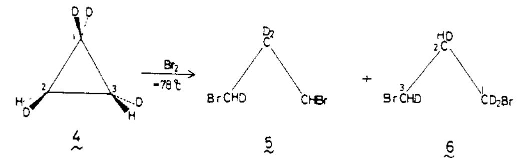
(1b)

The E-inversion process occurs in the reactions of the cyclopropanols with the brominating reagents (e.g., *N*-bromosuccinimide) (eq 2a):[5]



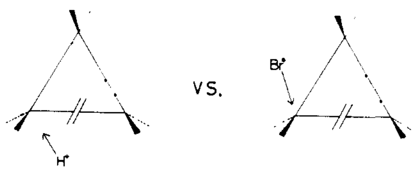
(2a)

A recent experiment (eq 2b) demonstrated that the bromination of the substituent-free CP is a double E,N-inversion process.[6] The product **6** has >85% of the erythro form. The stereochemistry will be discussed in the subsection of Zigzag Rearrangement.



4 **5** **6** (2b)

Thus, there is a marked contrast in the E-stereochemistry. A single mechanism cannot accommodate all the experimental data.[1e]



In this work, the ab initio MO calculations are made for the

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(1) (a) DePuy, C. H. *Fortsch. Chem. Forsch.* **1973**, *40*, 74. (b) DePuy, C. H. *Acc. Chem. Res.* **1968**, *1*, 33. (c) Collins, C. J. *Chem. Rev.* **1969**, *69*, 543. (d) Lee, C. C. *Prog. Phys. Org. Chem.* **1970**, *7*, 129. (e) Cristol, S. J.; Lim, W. Y.; Dahl, A. R. *J. Am. Chem. Soc.* **1970**, *92*, 4013. (f) Skell, P. S.; Day, J. C.; Shea, K. J. *J. Am. Chem. Soc.* **1976**, *98*, 1195.

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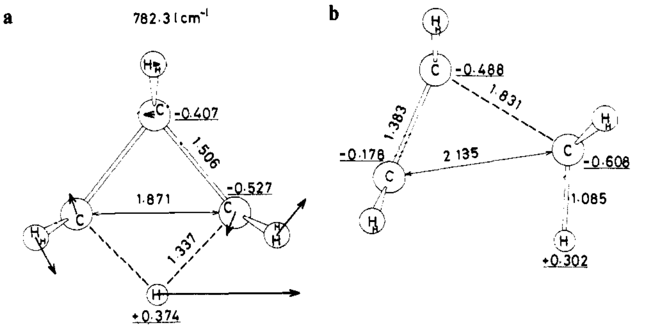

Figure 1. The structures of the protonated cyclopropanes with MIDI-1. The bond lengths and angles are in Å and deg, respectively. The underlined numbers denote the net atomic charges. In a, the reaction-coordinate vector of the sole imaginary frequency 782.3i cm^{-1} is depicted. Two "H" symbols in a circle indicate two out-of-plane hydrogen atoms.

systems of CP and E$^+$ to examine the E-dependent mechanism in detail.

Method of Calculation

SCF-MO calculations were carried out using the GAUSSIAN 80 program.[7] The MIDI-1 basis set[8] was used. It is of the contraction pattern (3321/321) on the chlorine, for example, and is of split-valence quality. To test the effect of polarization functions on MIDI-1 geometries, the MIDI-1$^{(*)}$ optimization is performed on cyclopropane and its Cl$^+$ adduct, $C_3H_6Cl^+$. The exponents of d orbitals of carbon and chlorine atoms in MIDI-1$^{(*)}$ are 0.61 and 0.56, respectively.

Stationary points in the reactions were searched for by the gradient method implemented in the program. Vibrational analyses of the stationary points were also made with MIDI-1 to judge whether they were equilibrium structures or the transition states. Thermochemical quantities, $H°$ and $S°$, were calculated by using standard equations of the statistical dynamics, the geometries, and the vibrational frequencies of the stationary points. These quantities are evaluated at the RHF level. The MP2 correction was included as the single point calculation [MP2//MIDI-1 and MP2//MIDI-1$^{(*)}$] because the correction to the Hartree–Fock total energy of CP is known to be significant.[2b]

The input data of the basis set, MIDI-1, are given in the supplementary material, Table A. Table B in the supplementary material gives all the geometries calculated in this work.

Results and Discussion

Protonation. The MIDI-1 optimized geometry of CP is in good agreement with the observed values. The C–C bond length is 1.512 Å (1.510) [1.503]. The C–H bond length is 1.075 Å (1.089) [1.084]. The HCH angle is 114.0° (115.1) [114.2]. The values in parentheses are experimental data,[9] and those in brackets are MIDI-1$^{(*)}$ optimized values.

The protonated CP has been extensively studied.[2] Two optimized structures are shown in Figure 1. The geometry of the structure in a was located under C_{2v} symmetry. The bridged structure was found to be a transition state for the proton shift. The reaction coordinate vector indicates that this movement leads to the more stable equilibrium structure b or the reaction intermediate. The proton is bound to a methylene group in structure b. The two C–C bonds are appreciably elongated, the other being shortened. Structure b is regarded as Mulliken charge-transfer (CT) complex between ethylene and the methyl cation.[2b]

The transition state in Figure 1a is not necessarily for the protonation of CP. The bare proton is far from the real electrophiles. We employed a hydronium ion to locate the transition state of the proton addition to CP in Figure 2. The smooth conversion of $H^+\cdots CP$ into the $C_2H_4 \rightarrow CH_3^+$ CT complex is clearly indicated.

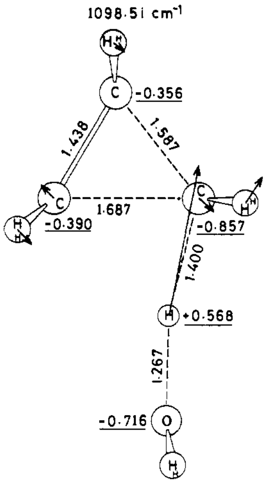

Figure 2. The geometry and the reaction-coordinate vector of the transition state of the proton transfer from hydronium ion to cyclopropane with MIDI-1.

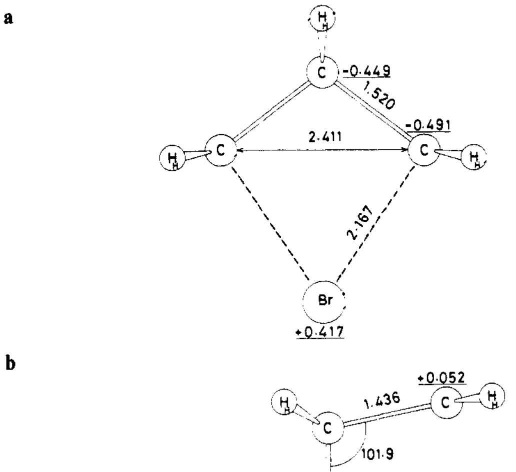

Figure 3. The equilibrium structures of Br$^+$ and cyclopropane. The notations are the same as in Figure 1 and are with MIDI-1.

The stereochemistry of the addition reactions of protic electrophiles is controlled by the CT complex intermediate (Figure 1b). The in-coming proton lies in the molecular plane. The front-side edge (2.135 Å) is longer than the back-side edge (1.831 Å). Dewar et al.[10] have very recently carried out MP4SDQ//6-31G* calculations to show a similar unsymmetrical structure (1.893 and 1.732 Å, respectively). Consequently, the ethylenic carbon on the same side of the in-coming proton is less anionic (–0.178). The subsequent nucleophilic attack preferentially occurs on this carbon.

The E-Retention Results. However, the possibility of the E-inversion cannot be ruled out. Prior to the nucleophilic attack, the methyl group is likely to migrate. In fact, the migration energy barrier is calculated to be less than 1 kcal/mol. Some substituents on the ethylenic carbons in the CT complex may reverse the relative lengths of the edges. In fact, DePuy et al.[11] showed that all *cis*-1,2,3-trimethylcyclopropane gives 32% E-inversion product. In any case, the nucleophiles are expected to attack on the back

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(7) GAUSSIAN 80: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, S.; Pople, J. A. *QCPE*, **1981**, 13, Program No. 406.

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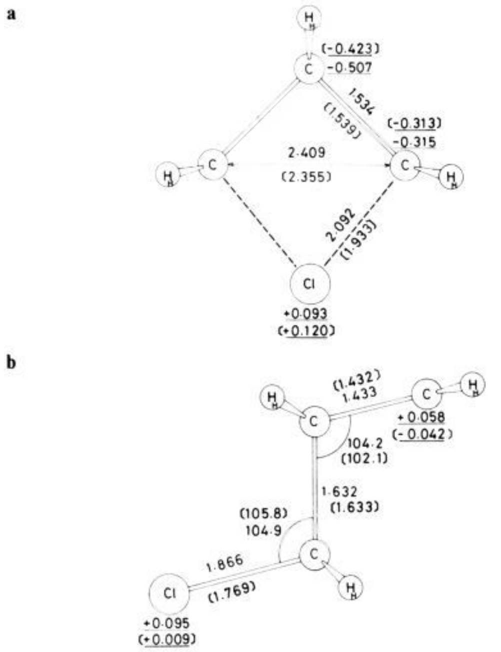
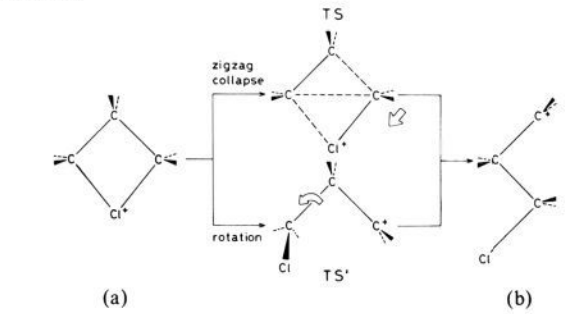


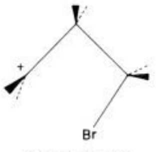
Figure 4. The equilibrium structures of Cl^+ and cyclopropane. All the vibrational frequencies (24) are calculated to be real for the isomers in a and b. The same notations as in Figure 1 are used. Numbers without and with brackets are MIDI-1 and MIDI-$1^{(*)}$ optimized distances, respectively.

side of the ethylenic moiety. The configuration is inverted (N-inversion). As a result, the prototype of the addition of the protic electrophiles to CP is the E-retention/N-inversion process. The double E,N-inversion process is a variation caused by the conformational change, the substituent effects, the nucleophilicity of the counter anions, and so on.

Halogenation. The system of Br^+ and CP was examined. The optimized geometries of the C_{2v} and C_s symmetries were shown in Figure 3. The C_{2v} geometry is a four-membered ring, trimethylene bromonium ion. The C_s geometry is of the classical open structure, 3-bromopropyl cation. In the cyclic bromonium ion, Br^+ is tightly bound to the carbons. The C–Br distance is 2.167 Å. The standard length is 1.93 Å. A crucial difference from the H^+–CP system was found. The C_{2v} structure is an equilibrium structure, or a reaction intermediate for the bromination. In contrast, this is the transition state for the protonation. Furthermore, the lowering of the symmetry from C_{2v} to C_s by shifting Br in the plane results in destabilization. No local energy minima were found for either CT complex or 3-bromopropyl cation of the eclipsed conformation. The equilibrium conformation of 3-bromocation is staggered (Figure 3b).

Scheme I





The Cl^+–CP system was also examined. The peculiar features of present interest are very similar to those of the Br^+–CP system, as is shown in Figure 4.

If the cyclic bromonium ion intermediate undergoes nucleophilic attack, the halogenation should be the E-retention/N-inversion process. This is incompatible with the experimental observations. Why does the halonium ion fail to react with the nucleophiles? This problem still remains open to question.

The back-side nucleophilic attack on the open cation of the staggered conformation can account for the observed double E,N-inversion. Here, a problem arises. Energetically, the cyclic bromonium ion is more stable than the 3-bromo cation (Table II). Therefore, the first step of the reaction is expected to yield the bridged cation. How does the cyclic four-membered ring halonium ion rearrange to the open structure? This is the subject of the following section.

Zigzag Rearrangement. The Br^+–CP system is too large to numerically examine the rearrangement. Encouraged by the similarity of the Br^+–CP to the Cl^+–CP system, we study the latter. This model is supported by the experimental evidence. The optically active *trans*-2-phenyl-1-methylcyclopropanol reacts with the chlorinating reagent to yield the product 4-chloro-4-phenyl-2-butanone, with the same stereochemistry as that of the brominating reagent.[5]

There are two routes (Scheme I) conceivable for the rearrangement of the cyclic four-membered chloronium ion to the 3-chloropropyl cation of the staggered conformation. The pre-

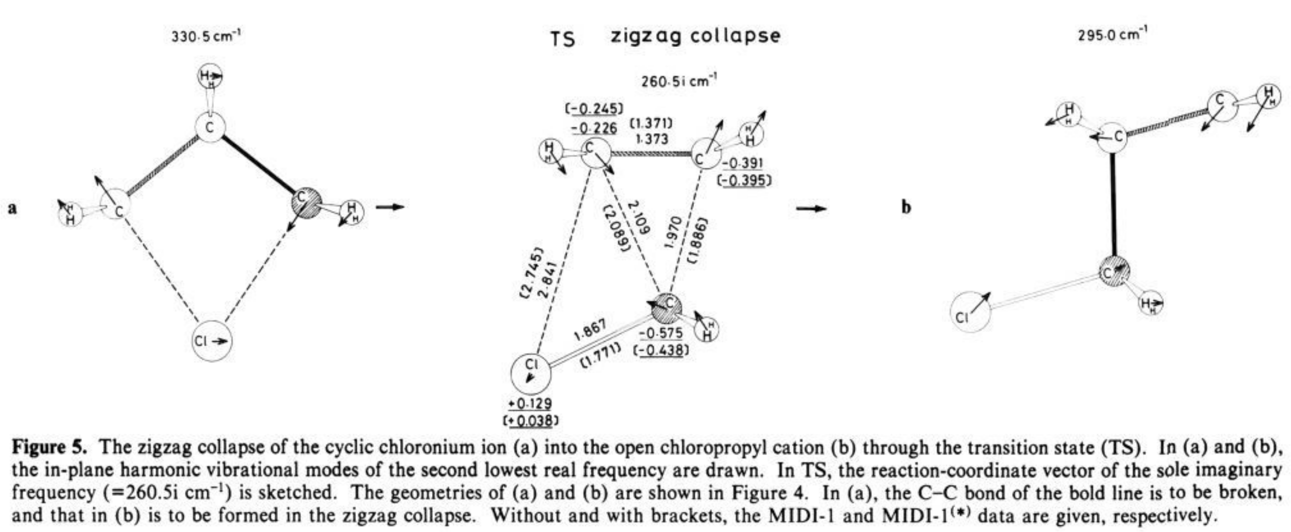


Figure 5. The zigzag collapse of the cyclic chloronium ion (a) into the open chloropropyl cation (b) through the transition state (TS). In (a) and (b), the in-plane harmonic vibrational modes of the second lowest real frequency are drawn. In TS, the reaction-coordinate vector of the sole imaginary frequency (=260.5i cm^{-1}) is sketched. The geometries of (a) and (b) are shown in Figure 4. In (a), the C–C bond of the bold line is to be broken, and that in (b) is to be formed in the zigzag collapse. Without and with brackets, the MIDI-1 and MIDI-$1^{(*)}$ data are given, respectively.

Table I. Energies Computed with the MIDI-1 Basis Set for Cyclopropane (CP) and E^+ (=H^+, Cl^+, and Br^+)[a]

species	figure showing the structure	E_T(RHF), au	E_T(MP2), au	ZP energy, kcal/mol	$H°$, au T = 298 K	$S°$, eu T = 298 K	$G°$, au T = 298 K
cyclopropane (CP)		−116.341 53	−116.611 92	54.77	−116.250 08	56.241	−116.276 80
		[−116.410 64]	[−116.801 41]				
Br^+		−2561.725 29	−2561.752 95				
Cl^+		−456.807 19	−456.841 80		−456.804 83	36.627	−456.822 23
		[−456.843 43]	[−456.947 03]				
H_3O^+		−75.849 60	−75.977 81	21.51	−75.811 34	46.617	−75.833 49
CP–H^+ ($C_3H_7^+$) of C_{2v} (bridged)	1a	−116.620 25	−116.887 84	59.89	−116.520 48	59.422	−116.548 71
CP–H^+ of C_s (open)	1b	−116.644 71	−116.907 42	60.98	−116.541 96	66.195	−116.573 41
CP–H_3O^+ (TS)	2	−192.209 66		74.56	−192.083 72	75.874	−192.119 77
CP–Br^+ of C_{2v}	3a	−2678.283 80	−2678.588 17				
CP–Br^+ of C_s	3b	−2678.264 31	−2678.555 61				
CP–Cl^+ of C_{2v}	4a	−573.412 04	−573.723 15	56.12	−573.317 09	68.520	−573.349 64
		[−573.539 10]	[−574.054 82]				
CP–Cl^+ of C_s	4b	−573.391 94	−573.694 95	55.08	−573.298 16	72.630	−573.332 67
		[−573.515 01]	[−574.018 52]				
CP–Cl^+ (TS)	5	−573.380 02	−573.696 66	54.71	−573.287 93	67.696	−573.320 09
		[−573.506 60]	[−574.021 29]				
CP–Cl^+ (TS')	6	−573.389 07	−573.694 72	55.01	−573.296 23	68.569	−573.328 81
		[−573.513 96]	[−574.021 83]				

[a] E_T is the total electronic energy in atomic unit. ZP energy stands for the zero-point energy in kcal/mol. Thermochemical data ($H°$, $S°$, and $G°$) are evaluated at the RHF level with MIDI-1. E_T(RHF)'s in brackets of CP and CP–Cl^+ correspond to MIDI-1(*) optimized geometries.

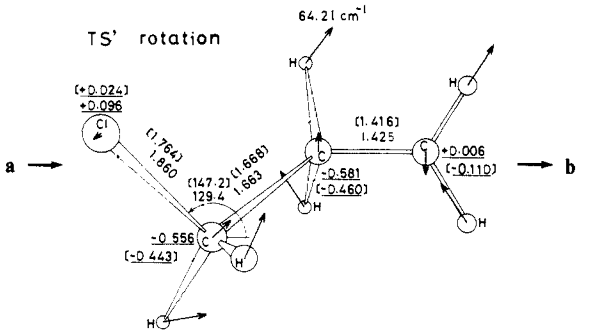


Figure 6. The transition state (TS′) of the rotation from the cyclic chloronium ion (a) to the open chloropropyl cation (b). In (a) and (b), the out-of-plane harmonic vibrational modes of the lowest frequency are 140.5 and 77.2 cm^{-1}, respectively. For TS′, the same notations as in TS of Figure 5 are used. One imaginary (=64.2i cm^{-1}) and 23 real frequencies are obtained in TS′, which demonstrates that TS′ is also a real transition state.

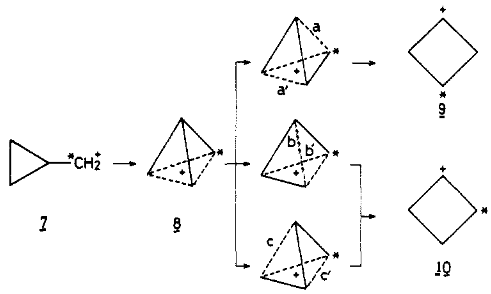
diction is based on the vibrational analysis of the four-membered ring intermediate. The in-plane antisymmetric stretching and the out-of-plane bending modes have very low frequencies (330.5 and 140.5 cm^{-1}, respectively) as shown in Figures 5 and 6. The same prediction can be made from the vibrational analyses of the product open cation. The in-plane distortion (295.0 cm^{-1}) and the rotation (77.2 cm^{-1}) are both low-frequency vibrations.

The in-plane motion suggests that the cleavage of one of the C–Cl bonds is accompanied by the C–C bond formation between the diagonal carbons and by the weakening of the C–C bond on the opposite side of the breaking C–Cl bond. The resulting structure is close to that of the CT complex between ethylene and the chloromethyl cation. Surprisingly, no local minima were located for the complex. The complex is not a reaction intermediate but a transition state. The rearrangement is an elementary process, where the four-membered ring collapses in a zigzag manner into the linear structure. The zigzag collapse gives the E-inversion product. On the other hand, the rotation yields the E-retention product.

The transition state for the zigzag collapse has been located as shown in Figure 5. The vibrational mode of sole imaginary frequency indicates the corresponding nuclear motion appropriate to the transformation. In the zigzag collapse, the MIDI-1(*) length (Å) of the shaded C–C bond changes, 1.539 (a) → 1.371 (TS) → 1.432 (b). At the transition state, the geometry is of the CT complex between ethylene and the chloromethyl cation. The failure to gain sufficient stabilization to be an intermediate may be attributed to the substituent effect. The lone pair on the halogen atom delocalizes to the carbocation center of the chloromethyl cation. The electron-accepting ability of the cation ($Cl–CH_2 \leftarrow C_2H_4$) is lowered.

The out-of-plane motion suggests that the weakening of a C–Cl bond is accompanied by the rotation of the halomethyl about the C–C bond. The transition state for the rotation process is shown in Figure 6. The sole imaginary frequency proves the transition state. The geometry is similar to the open structure (b) rather than the four-membered ring (a). The product-like geometry indicates the late transition state.

Scheme II



The zigzag intramolecular rearrangement of the four-membered rings as an elementary process has not been proposed in such an explicit manner, although a similar mechanism was suggested for the isomerization of the cyclopropylcarbinyl cation to the cyclobutyl cation (Scheme II).[12] The experimental study with the ^{14}C-labeled cyclopropylcarbinyl cation revealed that the three methylene groups of the starting material achieve a degree of equivalence at some point between reactants and products which is well (although not uniquely) accounted for by a "nonclassial" cationic intermediate of structure **8**.[13] Conversion of the intermediate to the cyclobutyl cation requires breakage at a and a′, at b and b′, or at c and c′. If the conversion is an elementary process, it is one of the zigzag rearrangements defined in our present work.

Calculated Energies. The energies obtained by the RHF and MP2 calculations with the MIDI-1 basis set are listed in Table I. The thermochemical data ($H°$, $S°$, and $G°$) are also included there. The energies relative to the lowest energy minimum for each substituent (H^+, Cl^+, and Br^+) are displayed in Table II. The energies, E_T, of the protonated cyclopropanes (CP·H^+), (a) and (b), of Figure 1 are compared. The transition state (a) lies

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(12) Gould, E. S. *Mechanism and Structure in Organic Chemistry*; H. Holt and Co.: New York, 1959; p 590.

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Table II. MIDI-1 Energies Relative to the Lowest Energy Minimum for Each Substituent (H^+, Br^+, and Cl^+) in kcal/mol[a]

species	ΔE RHF	ΔE MP2
CP-H^+ (C_{2v})	15.35	12.29
CP-H^+ (C_s)	0.0	0.0
CP-Br^+ (C_{2v})	0.0	0.0
CP-Br^+ (C_s)	12.23	20.43
CP-Cl^+ (C_{2v})	0.0 [0.0]	0.0 [0.0]
CP-Cl^+ (C_s)	12.61 [15.12]	17.70 [22.78]
CP-Cl^+ (TS)	20.09 [20.40]	16.62 [21.04]
CP-Cl^+ (TS')	14.42 [15.78]	17.84 [20.70]

[a] For CP-Cl^+, MIDI-$1^{(*)}$ energies are also given in brackets.

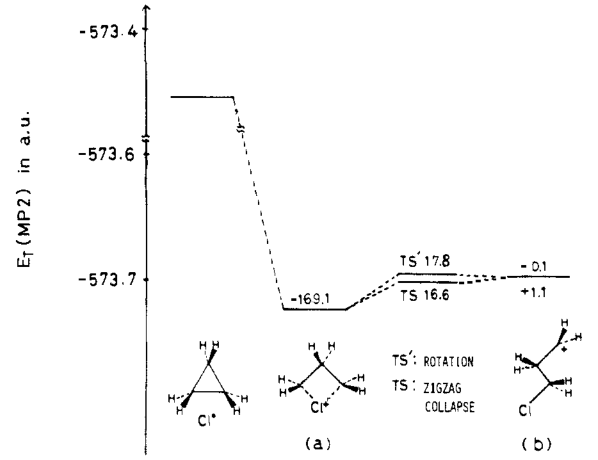
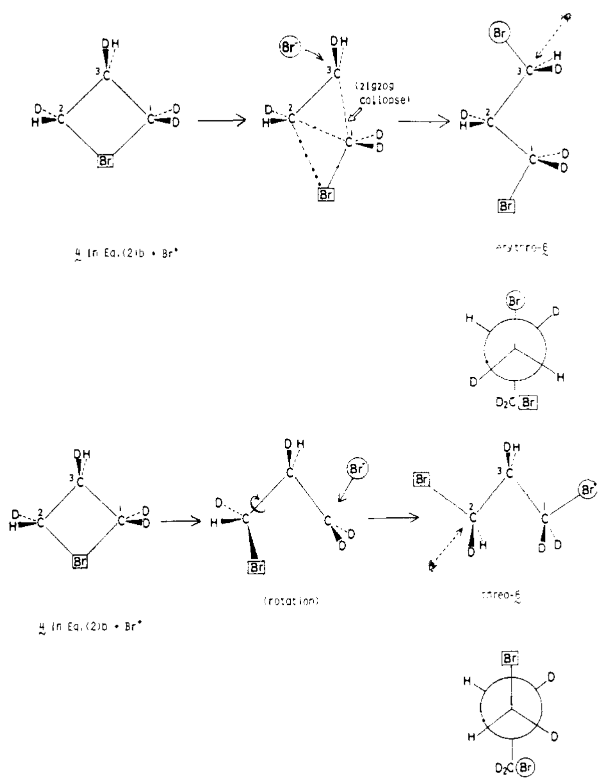


Figure 7. The energy variation of the CP and Cl^+ reaction based on the MP2//MIDI-1 calculations. The values are the energy differences from the left-hand stationary points in kcal/mol.

0.0245 au (15.3 kcal/mol) above the intermediate (b). The value is almost the same as the $G°$ difference (15.5 kcal/mol) and slightly larger than the MP2 E_T difference (12.3 kcal/mol). The CP·Br^+ system makes a striking contrast. The C_{2v} CP·Br^+ lies 0.020 au (12.2 kcal/mol) below the C_s geometry. The four-membered bromonium cation was shown not to be a transition state but an equilibrium structure. For CP·Cl^+, the RHF E_T difference is almost the same (12.6 kcal/mol) as that for the CP·Br^+. The replacement of CP·Br^+ by CP·Cl^+ to study the rearrangement is justified. The significant MP2 correlation correction effect was found in E_T. While the transition state (TS') for the rotation is 5.7 kcal/mol more stable than the TS for the zigzag collapse at the RHF level, the energy ordering is reversed (TS < TS', lower by 1.2 kcal/mol) at the MP2 level. This result indicates that the zigzag collapse occurs comparably to the rotation. In fact, the bromination to the unsubstituted CP in eq 2b supports the theoretical prediction of MIDI-1 (more than 85% *erythro*-6 produced).[6] Thus, the electron correlation effect is important when the CP reactivity is compared.[14] The energy variation along the reaction coordinate is depicted in Figure 7. The barriers to the rearrangements are 16–18 kcal/mol at MP2. In view of these values, two rearrangements are considered to be facile processes.[15]

The effect of the polarization functions, d orbitals on carbon and chlorine atoms, on the geometry, electronic distributions, and energies is examined. A noticeable geometric change by MIDI-1 → [MIDI-$1^{(*)}$] is the decrease of the C–Cl distance (~0.1 Å) in Figures 4, 5, and 6. For the electronic distribution in these figures, the polarity overestimated by MIDI-1 is moderated reasonably. In Table II, MP2 ΔE's of MIDI-$1^{(*)}$ are larger than those of MIDI-1. This change is ascribed to the tightening of the C_{2v} four-membered structure through MIDI-1 → MIDI-$1^{(*)}$.

Scheme III



Stability of Cyclic Halonium Ions. The proton attack on CP has been shown to give the π-complex between ethylene and the methyl cation. The complex is an intermediate. The edge-protonated CP is not an intermediate, but a transition state. The halonium ion forms the stable four-membered ring intermediates. What is the origin of the stability of the four-membered ring structure?

The CP·X^+ species may be regarded as a CT complex between trimethylene and the halonium ions. The important orbital interactions are shown in Figure 8a. The orbitals for the CT interaction are symmetric in (i), those for the back-CT interaction being antisymmetric in (ii). The cyclic interaction of the symmetric orbitals is insensitive to the shift of X^+. The small shift does not result in significant CT loss. On the contrary, the back CT involving the antisymmetric orbitals is sensitive to the X^+ shift. The small displacement causes a great destabilization. The extent of these interactions is proportional to the magnitude of the MO overlap. The MO overlap with the STO-3G basis set clearly demonstrates the difference between the symmetric and antisymmetric orbitals in the sensitivity toward the X^+ shift (Figure 8b). The back CT caused by the MO overlap (ii) was shown to be more important in determining the stabilities of the four-membered ring structures. When Cl^+ deviates from the C_{2v} axis, the MO overlap (ii) decreases considerably.

Various C_{2v} CP·X^+ model compounds (X = H, Li, F, Na, and Cl) were compared to substantiate the crucial role of the back CT. The calculated results are shown in Figure 9. Two low or imaginary frequencies of the harmonic vibrations are noteworthy. They are the in-plane antisymmetric mode (ν_{in}) and the out-of-plane symmetric mode (ν_{out}). For the halogens (X = F and Cl), the frequencies are both real, and the four-membered ring is an equilibrium structure. The structure corresponds to the transition state for X = H (one imaginary frequency) and to the "double saddle point" (two imaginary frequencies) for X = Li and Na.

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(14) At $T = 300$ K, assuming the product distribution of 90% erythro and 10% threo for simplicity, one may calculate $\Delta G = 1.3$ kcal/mol. The energy is in good agreement with our MP2 MIDI-1 $\Delta E = 1.2$ kcal/mol. However, this agreement is somewhat fortuitous. With MIDI-$1^{(*)}$, the MP2 $\Delta E = -0.3$ kcal/mol (in Table II). The exact evaluation of such a small energy difference is beyond the present computational accuracy. The solvent effect would also overwhelm the delicate comparison. In this work, the result that TS is as likely as TS' is postulated.

(15) At the end of the rearrangement of CP·Cl^+, the nucleophile Cl^- approaches the cationic methylene carbon. The formation of the C–Cl covalent bond (from $C^+ \cdots Cl^-$) stabilizes the system and makes the actual reaction more exothermic.

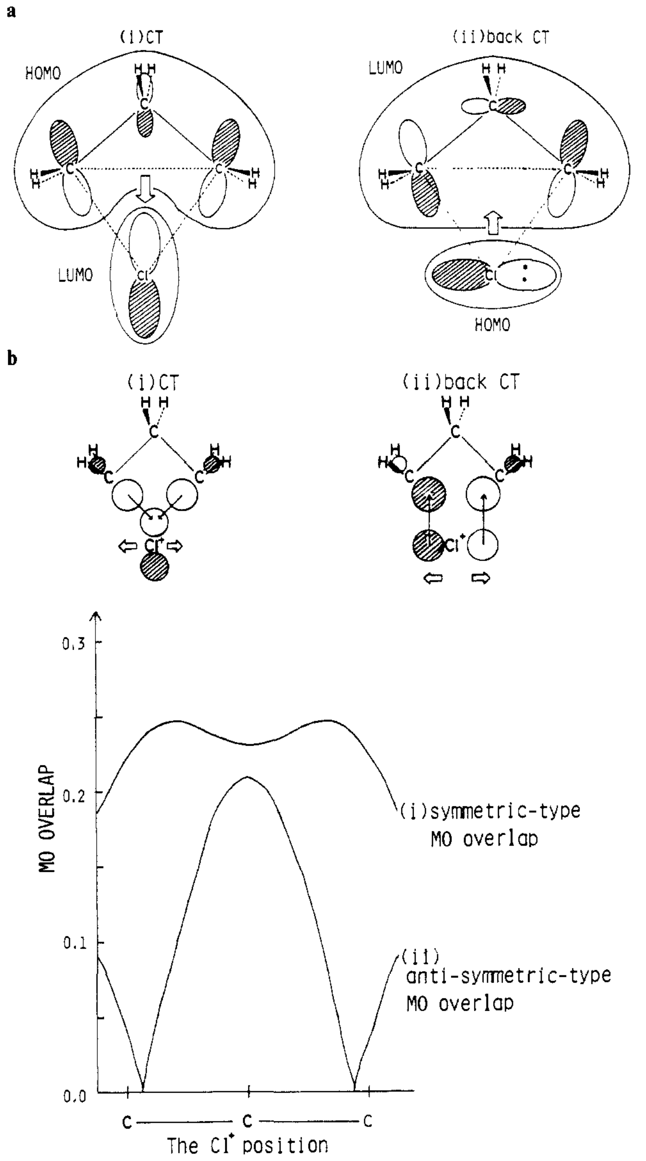


Figure 8. (a) Two charge-transfer (CT) interactions in the cyclic chloronium ion. (b) The change of two MO overlaps for the Cl$^+$ horizontal shift. (i) ∫HOMO(CP)·p_σ(Cl$^+$) d*v*; (ii) ∫LUMO(CP)·p_π(Cl$^+$) d*v*.

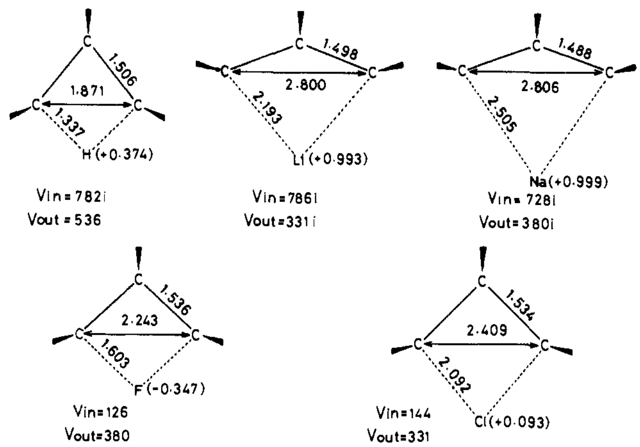


Figure 9. The MIDI-1 optimized C_{2v} geometries of CP·X$^+$ (X = H, Li, Na, F, and Cl). ν_{in} is the frequency (cm^{-1}) of the in-plane antisymmetric mode, and ν_{out} is that of the out-of-plane symmetric mode. Bond distances are in Å, and the numbers in parentheses are the net atomic charges.

The halonium ion has a p_π lone-pair orbital. The back CT can occur through this orbital. In H$^+$, Li$^+$, and Na$^+$, no antisymmetric occupied orbitals are available at high energy levels. The back CT is ineffective. Thus, the back CT or the antisymmetric orbital interaction maintains the four-membered ring structure.

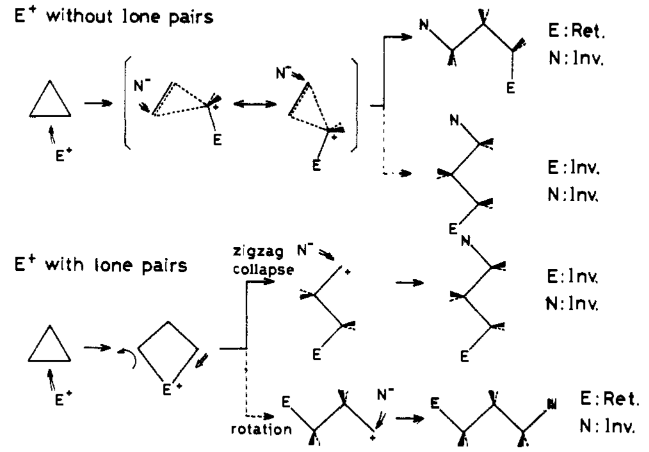
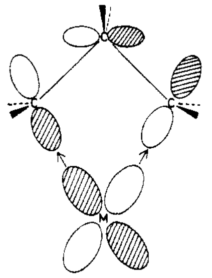


Figure 10. Schematic representation of the stereochemical course in the electrophilic addition reactions to cyclopropane.

There are some experimental studies of the CP ring opening by platinum,[16a] palladium,[16b] and mercury complex.[16c] The structure of the four-membered ring, platinum metallacycle,[17] has been recently found to be similar to that of palladacyclobutane.[18] The stability of the four-membered metallacycles is ascribed to the (d_π → CP) back CT.



The process of the four-membered ring formation and the subsequent zigzag collapse seems to be applicable to the CP ring opening by metal complexes. For instance, the reaction of mercury(II) acetate, Hg(OAc)$_2$, with cyclopropanols has been reported to give the inversion of configuration at the point of the electrophilic attack.[16c] The complex CP···HgOAc$^+$ would be the precursor for the zigzag process.

Conclusion

The electrophilic cleavage of cyclopropane has been investigated by the ab initio molecular orbital calculations. For the electrophiles (e.g., H$^+$) without p_π lone-pair orbitals, the reactions take place via the π-complex intermediates (e.g., ethylene···methyl cation) where the front-side C–C bond of CP and one of the back-side bonds are weakened. The nucleophiles are expected to attack on the back side of the complexes (N-inversion). The nucleophilic attack on the ethylenic carbon closer to E results in the E-retention. The attack on the farther carbon leads to the E-inversion. The geometry of the π-complex is unsymmetrical. The closer carbon attack is preferential. The prototype of the addition reactions of the protic electrophiles with CP is the E-retention/N-inversion process. The double E,N-inversion is a secondary version caused by other factors, e.g., substituents, solvents, and so on.

For the electrophiles (e.g., halonium ion) with the p_π lone-pair orbitals, the first intermediate is the cyclic four-membered ring

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ions. The stabilities of the ring structures are due to the back CT or antisymmetric orbital interaction. The next step is the zigzag collapsing of the intermediates. This is an elementary process. The following nucleophilic attack leads to the double E,N-inversion. The proposed schemes are summarized in Figure 10.

The electrophilic edge attack has been believed to give the E-retention product. The most important finding here is that the edge attack may give the E-inversion product through the zigzag collapse of the edge attack intermediates.

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Registry No. CP, 75-19-4; H^+, 12408-02-5; Cl^+, 24203-47-2; Br^+, 22541-56-6.

Supplementary Material Available: Tables of exponents and coefficients of the MIDI-1 basis set given as the GAUSSIAN 80 or 82 input data and molecular Cartesian coordinates (12 pages). Ordering information is given on any current masthead page.

Superacid Solutions in Hydrogen Fluoride

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Abstract: The Hammett acidity function, H_0, has been determined for solutions of H_2O, KF, HSO_3F, PF_5, TaF_5, NbF_5, AsF_5, and SbF_5 in anhydrous HF, using a set of aromatic nitro compound indicators. The H_0 value for anhydrous HF was found to be −15.1 rather than −11 as previously believed. It was confirmed that water is not fully ionized as a base. The values of H_0 show that solutions of SbF_5 in HF are much more acidic than solutions of SbF_5 or $SbF_5{\cdot}3SO_3$ in HSO_3F.

It has long been recognized that solutions of antimony pentafluoride and some other pentafluorides in anhydrous HF are very highly acidic media. In this paper we present the results of some quantitative studies of the acidity of such media in terms of the Hammett acidity function, H_0, for solutions of KF, H_2O, SbF_5, AsF_5, NbF_5, TaF_5, and HSO_3F in anhydrous HF. We have used the same set of nitro aromatic weak-base indicators that we used for our earlier measurements[1,2] of the acidities of solutions in sulfuric acid and fluorosulfuric acid and some weaker bases of the same type.

On the basis of the ability of HF solutions of SbF_5, AsF_5, NbF_5, and PF_5 to dissolve CoF_3 and the metals Cr, Mg, and Mn, Clifford et al.[3-5] concluded that the acid strength of these pentafluorides decreased in the order $SbF_5 > AsF_5 > NbF_5 > PF_5$. McCaulay et al.[6] measured the ability of solutions of NbF_5, TaF_5, and PF_5 in HF to extract *m*- and *p*-xylene from *n*-heptane, and they concluded that the order of acid strengths was $TaF_5 > NbF_5 > PF_5$.

Kilpatrick and Lewis[7] made the first quantitative study of solutions of antimony pentafluoride in HF, and from their measurements of the electrical conductivity of dilute solutions of SbF_5 they concluded that SbF_5 is a strong acid ionizing according to the equation

$$SbF_5 + 2HF \rightarrow H_2F^+ + SbF_6^-{}_6$$

Further conductivity measurements by Hyman et al.[8] and by Gillespie and Moss[9] and cryoscopic measurements by Gillespie et al.[10] confirmed that SbF_5 is fully ionized in dilute solution in HF. But ^{19}F NMR studies[9] showed that, except in the most dilute solutions, increasing amounts of the polymeric ions $Sb_2F_{11}^-$, $Sb_3F_{16}^-$, etc., are formed with increasing concentration of SbF_5. Gillespie et al.[10] also showed that PF_5 is a nonelectrolyte and that at low temperatures AsF_5 is extensively ionized, although not fully, according to the equation

$$2AsF_5 + 2HF \rightleftharpoons H_2F^+ + As_2F_{11}^-$$

The Hammett acidity function for the H_2O–HF system has been studied by several groups of workers[11-13] and their results are shown in Figure 1. There is a sharp increase in $-H_0$ in the vicinity of 100% HF which is similar to that observed in the H_2SO_4–HSO_3F system in the vicinity of 100% HSO_3F.[2] This rapid increase in $-H_0$ is due to the rapidly increasing concentration of the solvated proton, H_2F^+ or $H_2SO_3F^+$, arising from the solvent autoprotolysis. This has meant that the value of H_0 for 100% HF has been very difficult to determine because very small concentrations of basic impurities such as water can drastically decrease the value of $-H_0$. We show later that, for this reason, the previously reported value[12,13] of $-H_0 = -11$ is too low.

There have been two previous studies of the acidity of solutions of SbF_5 in HF. Tremillion et al.[14] have measured the acidity of 1 M solutions of NaF and SbF_5 and some other pentafluorides in terms of the *R*(H) function using a chloranil electrode. They reported values of *R*(H) of 14.2 for 1 M NaF and 27.9 for 1 M SbF_5. Sommer and his collaborators[15] have obtained values of H_0 by studying the protonation of *p*-methoxybenzaldehyde by means of ^1H and ^{13}C NMR. The results of these earlier studies of SbF_5 solutions are discussed later together with our own.

Experimental Section

Hydrogen Fluoride. Anhydrous hydrogen fluoride (Harshaw Chemical Co.) was purified by fractional distillation with a column of the type described by Shamir and Netzer[16] in conjunction with a Monel and

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