An MO Calculation of the Reaction Path of a Symmetry-Disfavored 1,3-Sigmatropic Rearrangement

Tsutomu Minato, Satoshi Inagaki, Hiroshi Fujimoto, and Kenichi Fukui
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

(Received September 8, 1976)

The path of suprafacial 1,3-sigmatropic rearrangement is studied with the INDO-CI and INDO LMO methods. The methyl migration has been found to be represented by successive 1,2-shifts with a biradicaloid transition state. The interaction between the singly occupied MO's of allyl and methyl fragments is suggested to be responsible for the determination of the path. A subsidiary orbital also plays a part. On the other hand, the chlorine migration has been shown to be a direct 1,3-shift. The interaction between the lowest unoccupied MO of the allyl cationic part and the highest occupied MO of the remaining part, chloride anion, has been found to govern the path of chlorine migration. The lone pair electrons of the migrating fragment makes the successive 1,2-shifts quite unlikely in the 1,3-suprafacial chlorine rearrangements.

The frontier orbital theory[1] and Woodward-Hoffmann rule[2] have been demonstrated to be useful in disclosing the electronic control of chemical reaction paths. On the other hand, some interesting suggestions[3] have been presented on the mechanism of the reactions which do not obey the prediction obtained from the usual orbital symmetry considerations. In this paper, the mechanistic difference between the suprafacial 1,3-sigmatropic migrations of a methyl group and a chlorine atom over the allylic framework will be studied on the basis of a semiempirical all-valence electron MO calculation.

Recently, there have been several notable developments in the study of 1,3-sigmatropic rearrangements. According to the Woodward-Hoffmann rule, 1,3-sigmatropic rearrangements should occur in a suprafacial fashion over the allylic framework with the inversion of the configuration of the migrating group, or in an antarafacial fashion with the retention of the configuration of the migrating species. Experiments do show, however, that some thermal suprafacial 1,3-sigmatropic reactions take place with retention.[4] On the other hand, intramolecular chlorine migration was observed in allyl chloride.[5] If the single chlorine p orbital participates in the rearrangement, the 1,3-migration would be a symmetry-disfavored process. There have been some MO calculations[6] on the mechanisms of the 1,3-migrations. However, the reaction paths have not been discussed in detail as yet. Accordingly it may be worthwhile to study the mechanism of the 1,3-sigmatropic rearrangements based on the detailed information on the possible course of the migration.

We studied first the paths of the 1,3-methyl and chlorine migrations over the allylic framework by the use of the INDO MO method. Then, the bond interchange along the reaction path was examined in terms of the localized molecular orbital (LMO) to get a clearer insight into the formation and breaking of chemical bonds which are characteristic of the migrations.

Method

The INDO approximation[7] is employed in the present MO calculation. The reaction system consists of an allyl and a methyl fragment and of an allyl and a chlorine fragment. The geometrical parameters of allyl and methyl fragment were taken after the standard values proposed by Pople.[7a] Three typical pathways of a suprafacial 1,3-sigmatropic reaction, depicted in Fig. 1, have been examined tentatively. In the first model, Route 1, the migration occurs along the line connecting C_1 and C_3 of the allylic framework. The second is Route 2 in which the migrating group (M) approaches first to C_2, and then moves on to C_3. In Route 3, M transfers from C_1 to C_3 far away from C_2. The energies of the two reaction steps, Step 1 and Step 2, for each of the models, Route 1—3, were compared. Figure 1 illustrates the variables representing the reaction systems. Two independent parameters, R_1 and R_2 were selected. R_1 represents the height of M above the plane of the allylic framework. R_2 stands for the vertical distance between the point of the projection of M onto the allylic plane and the line connecting the two terminal carbons (C_1 and C_3) of the allylic framework. The origin of the coordinate system is taken at the midpoint of C_1 and C_3. The minus sign of R_2 means that M moves away from the origin in the opposite direction to C_2. Step 1 corresponds to the initial stage of the reaction. Namely, M is above the

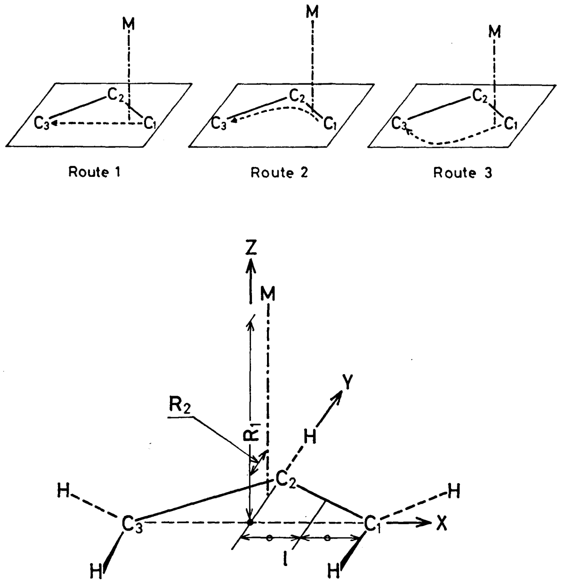


Fig. 1. Assumed reaction models. The origin of the coordinate system is on the center of C_1–C_3 line.

TABLE 1. TOTAL ENERGY OF METHYL MIGRATION

	R_1	R_2	Total energy	Total energy with CI
Step 1	1.50 Å	0.00 Å	−907.46 eV	−907.75 eV
	1.50	0.175	−907.56	−907.84
	1.50	0.35	−907.32	−907.57
	1.40	0.00	−907.45	−907.76
	1.40	0.175	−907.45	−907.77
	1.40	0.35	−907.15	−907.46
Step 2	1.50	0.00	−904.93	−905.36
	1.50	0.35	−905.22	−906.07
	1.50	0.70	−904.25	−905.31
	1.40	0.00	−905.37	−905.86
	1.40	0.35	−904.97	−905.79
	1.40	0.70	−903.68	−904.75

TABLE 2. TOTAL ENERGY OF CHLORINE MIGRATION

	R_1	R_2	Total energy
Step 1	1.80 Å	−0.35 Å	−1073.45 eV
	1.80	−0.175	−1073.46
	1.80	0.0	−1073.37
	1.80	0.175	−1073.18
Step 2	1.80	−0.70	−1071.51
	1.80	−0.525	−1071·59
	1.80	−0.35	−1071.52
	1.80	0.0	−1070.95

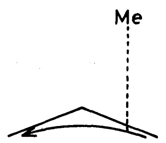
line (l) which is perpendicular to the line connecting C_1 and C_3 with X= one-fourth of C_1–C_3 length. Step 2 represents the transition state, and M is placed above the Y-axis. Total energies of the system are listed in Tables 1 and 2.

The Reudenberg-Edmiston LMO's[8] used in Steps 1 and 2 were calculated to investigate the change in the chemical bonds during the reaction. The bond orbitals obtained visualize the appearance and disappearance of specific bonds along the reaction process, as will be seen in the next section.[9]

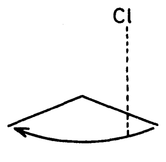
Results

From the results of the INDO calculation without configuration interaction (CI) given in Table 1 it is seen that Route 2 is adequate for representing the methyl migration at the initial stage but is not suitable for describing the transition state. However, the result with CI suggests that the reaction path would be close to Route 2 throughout the migration. These results indicate that the inclusion of the CI is of essential significance in obtaining reasonable results in regard to the loosely bound transition state. The gross atomic charges given in Table 3 show that the methyl and allyl fragments tend to be neutral at the transition state (R_1=1.50 Å, R_2=0.35 Å).

The most stable geometry for the chlorine migration was found to be R_1=1.80 Å and R_2=−0.175 Å in Step 1, and R_1=1.80 Å, R_2=−0.525 Å in Step 2, as shown in Table 2: that is, the reaction path is close to Route 3. It should be noted that the path is very different from that of the methyl migration mentioned above. The chlorine migrates along the pathway as to minimize the interaction with C_2 of the allylic framework. In the chlorine migration the inclusion of the CI did not show any serious change in our conclusion, so the CI result was omitted in Table 2. The electron populations given in Table 3 show that the transition state of the chlorine migration is likely to be an ion-pair.



The methyl migration.



The chlorine migration.

The LMO's of the methyl migration are illustrated in Fig. 2. It is found that the LMO's localized in C–H bonds do not change markedly throughout the migration. The methyl carbon (C_M)–C_1 bond which disappears in the reaction is transformed into a three-centered bond, C_1–C_M–C_2, and the double bond (C_2=C_3) is represented by two bent bonds in Step 1. In Step 2 one of the bent bonds of C_2=C_3 is transformed into the three-centered bond(C_2–C_M–C_3), and the other bent bond is converted to a σ-bond (C_2–C_3). Accordingly, two three-centered bonds appear in Step 2. The LMO's of the doubly-excited configuration were also calculated. The doubly-excited configuration in which a pair of electrons are promoted from the highest occupied (HO) MO to the lowest unoccupied (LU) MO of the whole system was found to be the most important one from the CI calculation. Figure 3 illustrates several LMO's of the doubly-excited configuration in Step 2. One of the two three-centered bond orbitals is converted to the C_M–C_2 bond and the other is transformed to the orbital which localizes at C_1 and C_3. This localized orbital at C_1 and C_3 seems to represent the biradical nature of the system. The transition state has been found from the CI calculation to be described sufficiently well by the linear combination of the ground configuration and the doubly-excited configuration mentioned above. It is concluded, therefore, that the transition state of the methyl migration possesses a biradical character to a certain extent.

The LMO's for the chlorine migration are illustrated in Figs. 4 and 5. It is seen that the LMO's localized in the C–H bonds are not changed markedly throughout the migration. Figure 4 demonstrates that the mode

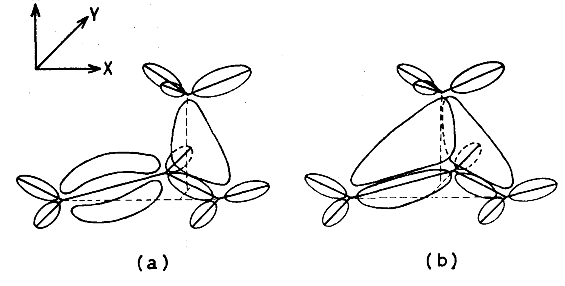


Fig. 2. The schematic presentation of the LMO's of the methyl migration. (a): Step 1. (b): Step 2.

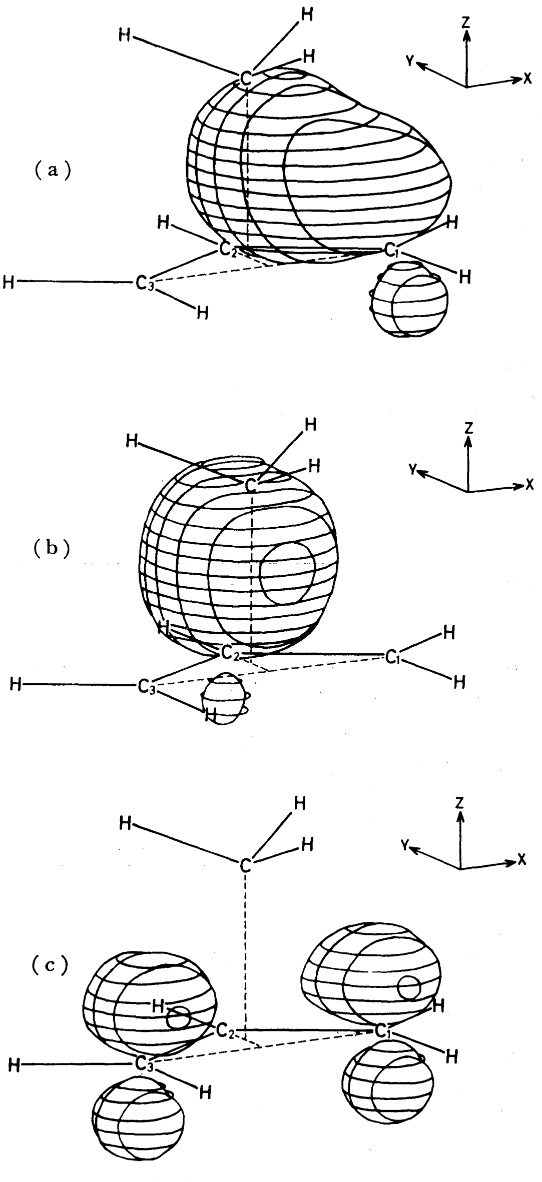


Fig. 3. The particular LMO shapes of the methyl migration. The density line is 0.3 e/Å^3. (a): One of the three-centered bonds of the ground configuration at the transition state. (b): One of the LMO's of the doubly-excited configuration at the transition state. (c): Another LMO of the doubly-excited configuration at the transition state.

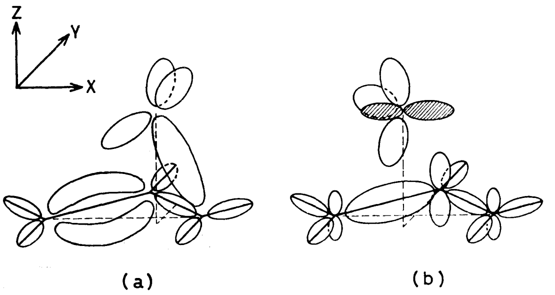


Fig. 4. The schematic presentation of the LMO's of the chlorine migration. (a): Step 1. (b): Step 2. Two shaded lobes which are nearly equal to chlorine 3p$_x$ AO represent one of the chloride anion lone pairs, and one LMO is composed of three 2p$_z$ Ao's of the allyl carbons.

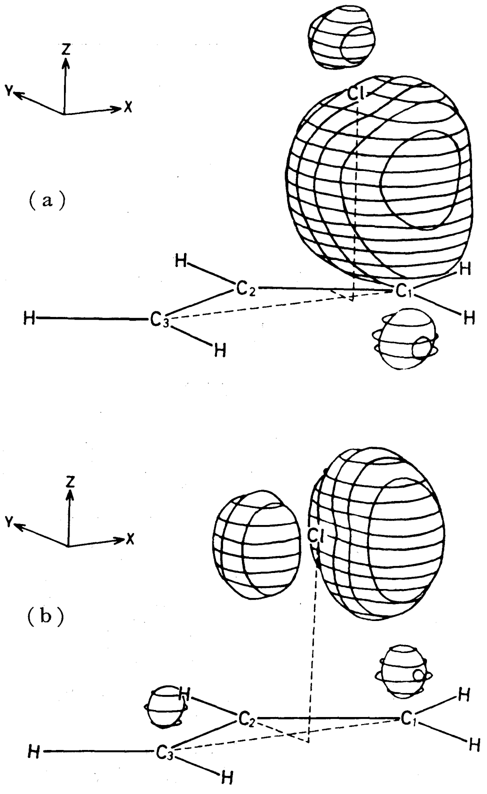


Fig. 5. The particular LMO shapes of the chlorine migration. The density line is 0.3 e/Å^3. (a): C_1–Cl bond orbital of Step 1. (b): C_1–Cl–C_3 bond orbital of Step 2.

of bond interchange in the chlorine migration is different from that in the methyl migration. In the case of the chlorine migration, one of the bent LMO's representing C_2=C_3 bond is transformed into the LMO composed of three 2p$_z$ atomic orbitals (AO's) of allyl carbons. The chlorine atom is bonded to C_1 and C_3 of the allylic framework by the LMO corresponding to the chlorine lone pair at the transition state. However, the LMO representing C_1–Cl–C_3 three-centered bond is almost exclusively localized at the chlorine 3p$_x$ AO and, hence, the migrating chlorine is bound to the allylic framework very weak in the neighborhood of the transition state. The gross charges on the composed atoms and groups shown in Table 3 indicate that the transition state should be described as an ion-pair between the allyl cation and chloride ion, in agreement with the result of the LMO calculation.

We may conclude here from our INDO-CI and LMO calculations that the suprafacial migration of methyl with retention of the configuration of the migrating center, takes place *via* successive 1,2-shifts. However, the migration possesses a single symmetrical transition state and, hence, it should be classified as a one-step process. On the contrary, the chlorine migration is concluded to occur by way of a direct 1,3-shift with an ion-pair transition state.

Table 3. Atomic gross charge at the transition state

The optimized geometry without CI (R_1=1.40 and R_2=0.0) of the methyl migration.

	Allyl carbon			Allyl group	Methyl carbon	Methyl group
	C_1	C_2	C_3			
Gross charge	−0.187	0.229	−0.187	−0.153	0.394	0.153

The optimized geometry with CI (R_1=1.50 and R_2=0.35) of the methyl migration.

	Allyl carbon			Allyl group	Methyl carbon	Methyl group
	C_1	C_2	C_3			
Gross charge without CI	−0.172	0.211	−0.172	−0.142	0.333	0.142
Gross charge with CI	−0.162	0.203	−0.162	−0.131	0.311	0.131

The optimized geometry (R_1=1.80 and R_2=−0.525) of the chlorine migration.

	Allyl carbon			Allyl group	Chlorine
	C_1	C_2	C_3		
Gross charge	0.143	0.043	0.143	0.400	−0.400

Discussion

Let us interpret here the reaction mechanisms of the methyl and chlorine migrations by means of the orbital interaction in order to disclose the reason why the paths of the migrations are different from each other.

Methyl Migration. The principal orbital interactions involve the three π orbitals (π_1, π_2, and π_3) of the allyl group, and a σ-type (ψ_σ) and a π-type (ψ_π) orbitals of the methyl group as shown in Fig. 6. The interaction of ψ_σ with π_1 and π_3 gives ψ_1, ψ_4, and ψ_5, and that between π_2 and ψ_π gives ψ_2 and ψ_3. The CI coefficients of the lowest closed-shell configuration and the $\psi_3 \rightarrow \psi_4$ doubly-excited configuration are listed in Table 4, as well as the orbital energies of ψ_3 and ψ_4. The contributions of the other excited configurations are found to be negligibly small. The MO ψ_4 has a bonding nature between C_2 and C_M, but the MO ψ_3 is antibonding. Accordingly, the mixing in of the $\psi_3 \rightarrow \psi_4$ doubly-excited configuration gives rise to the strengthening of both the σ and π type bondings in the reaction system. Table 4 clearly indicates that the effect of the CI becomes more significant as the separation between the methyl carbon and C_2 gets smaller.

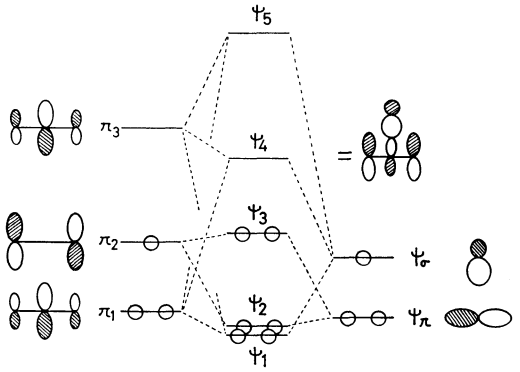


Fig. 6. The MO interaction diagram at the transition state of the methyl migration.

Table 4. The CI boefficients and orbital energy at the transition state of the methyl migration

R_1	R_2	C_0	$C_{3\rightarrow4}$	ψ_3	ψ_4
1.50 Å	0.70 Å	0.934	0.352	−6.99 eV	2.39 eV
1.50	0.35	0.950	0.309	−6.72	3.31
1.50	0.0	0.979	0.192	−6.31	4.14

The enhancement of mixing in of the diexcited configuration is attributable to the decrease in the energy gap between ψ_3 and ψ_4. The interaction between ψ_σ and π_1 stabilizes the system.[3a)] On the other hand, the interaction between ψ_σ and π_3 leads to the lowering of the ψ_4 orbital. It is obvious that the dominant component of ψ_4 is π_3. The interaction between ψ_σ and π_3 contributes to the stabilization of the transition state, as well as the interaction between ψ_σ and π_1, through the lowering of the composite MO ψ_1.

Berson and Salem introduced the subjacent orbital effect in order to explain the occurrence of the formally symmetry-disfavored 1,3-migrations. They claimed that this resulted not from an effect on the HOMO but instead from the interaction of the carbon p orbital with a subjacent, bonding allyl orbital.[3a)] We feel, however, that the interaction of the carbon p orbital with a subjacent orbital (π_1) was over-emphasized in their discussion. Since the carbon p orbital can interact both with π_1 and π_3, the role of π_3 orbital should be clearly recognized.[10)] Our INDO-CI calculation disclosed not only the importance of the depression of ψ_1 as the major stabilization through the direct overlap interaction between ψ_σ and π_1 but also that of ψ_4 for lifting the destabilization due to ψ_3 through the mixing in of the $\psi_3 \rightarrow \psi_4$ doubly-excited configuration to facilitate the occurrence of the migration.

The mechanism of 1,3-sigmatropic shift was rationalized above as a successive 1,2-shift. The interaction between the singly occupied (SO) MO of the allyl and the SOMO of the methyl is considered to have a key importance in stabilizing the reaction system at the initial stage of the migration. As the migration proceeds, however, the stabilization decreases because of the out-of-phase overlapping of ψ_σ with the C_3 lobe of the antisymmetric π_2 becomes large. Accordingly, the reaction would proceed along the pathway in which the C_3 lobe and ψ_σ tend to overlap as little as possible. That is, the migration seems to take the pathway in which the destabilization due to the weakening of the SOMO-SOMO interaction is as small as possible. Furthermore, the reaction should take place in a way as to give a large overlapping between ψ_σ and π_1. At the transition state the interaction of ψ_σ with π_1 and π_3 orbitals is important. Since the π_1 and π_3 MO's possess the largest amplitudes at the central carbon, the methyl group comes closer to C_2 to create larger overlaps of ψ_σ with π_1 and with π_3. The reason why Route 2 is the most favorable pathway is thus clarified.

The preference of the 1,2-shift to the direct 1,3-shift is explained in another way by considering the orbital interaction between the π bond (C_2–C_3) and the σ-bond (C_1–C_M) to be broken.11) The reaction may be initiated by the charge-transfer interaction from the former to the latter and *vice versa*. The mode of the orbital interaction between the HOMO and the LUMO of the two localized bonding regions is depicted in Fig. 7. It is seen that the overlapping of the HOMO of the C_2–C_3 π bond with the LUMO of the C_1–C_M σ bond is ineffective, while the overlapping of the LUMO of the former with the HOMO of the latter is effective. It is now obvious that the overlap interaction between the HOMO of the C_1–C_M bond and the LUMO of the C_2–C_3 π bond in this migration makes a successive 1,2-shift more likely than a direct 1,3-shift. This explanation leads to an important prediction that the 1,3-sigmatropic rearrangement with retention will occur easily when the migrating group has an electron donating group.12)

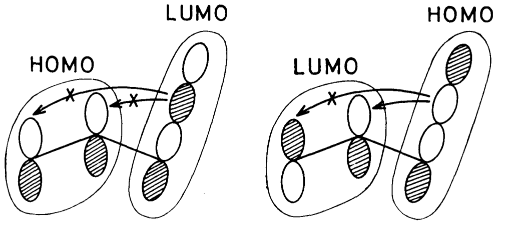
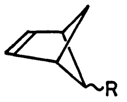
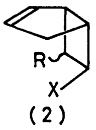


Fig. 7. The mode of the orbital interaction between the two bonding region.

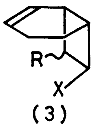
The mechanism presented here (a successive 1,2-shift) agrees with the experimental results in regard to the stereoselectivity of the migrating center.4c) The rate ratio of the 1,3-suprafacial rearrangement with retention to the rearrangement with inversion increases in the order bicyclo[2.1.1]hexene series (1)<bicyclo[3.2.0]-heptene series (2)<bicyclo[4.2.0]octene series (3)< monocyclic series (4).13)



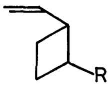
(1)



(2)



(3)



(4)

Berson and Holder4c) proposed that this rate ratio might depend on the reactant structures. Namely, they suggested that the overlap between the front lobe of the migrating carbon and the suprafacial lobe of the central carbon of the allylic framework would stabilize the transition state of the symmetry-disfavored reactions. The Berson's interpretation is consistent with our conclusion derived here, *i.e.*, the suprafacial 1,3-shift with retention of the configuration can be interpreted in terms of a successive 1,2-shift, because the facility of a 1,2-shift is also dependent upon the reactant structure.

Chlorine Migration. The orbital interaction of Step 2 was examined in a similar way as that of the methyl migration. The principal orbital interaction seems to include the three π orbitals of the allylic framework and chlorine $3p_x$ and $3p_z$ AO's. From the gross charges in Table 3, it is appropriate to consider here the orbital interaction between an allyl cation and a chloride anion. The MO interaction diagram is presented in Fig. 8. It is noted that the ψ_3 and ψ_4 MO's are interchanged in chlorine migration in comparison with the case of methyl migration. This is a reason why the inclusion of the CI does not change seriously the conclusion derived from the results of calculation without CI. The MO ψ_3 of the chlorine migration was found to have antibonding character between Cl and C_2 in the transition state. This means that the interaction between $3p_z$ AO and π_1 is greater than that between $3p_z$ AO and π_3. The difference in the ordering of the ψ_3 and ψ_4 levels between methyl and chlorine migrations is attributed to the lower energy of the chlorine $3p_z$ AO than that of the ψ_σ MO of the methyl group. Figure 8 shows that the interaction between the HOMO ($3p_x$ AO) of the chloride anion and the LUMO (π_2) of the allyl cation stabilizes the transition state effectively.

The path of the 1,3-migration of chlorine is rationalized in the following manner. The interaction between the π_2 MO and the $3p_z$ AO has a key importance in stabilizing the reaction system at the initial stage of the migration. As the migration proceeds, however, the stabilization decreases because the out-of-phase overlapping of $3p_z$ AO with the C_3 lobe of the antisymmetric π_2 becomes large. However, throughout the chlorine migration reaction, unlike the methyl migration, the interaction between π_2 and $3p_x$ AO is bonding in character to stabilize the system efficiently. The interaction between π_1 and $3p_z$ AO is larger than that be-

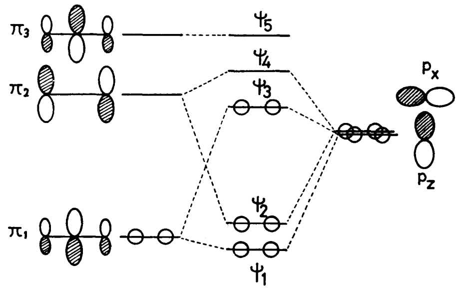
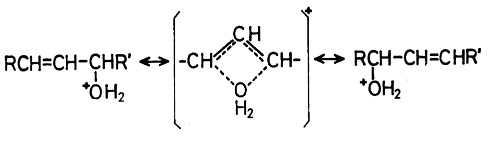


Fig. 8. The MO interaction diagram at the transition state of the chlorine migration.

tween π_3 and $3p_z$ AO as mentioned above. Consequently, the interaction of $3p_z$ with π_1 and π_3 leads to the destabilization of the reaction system. The destabilization makes the chloride anion migrate in such a way as to minimize the overlap with C_2. The reason why Route 3 is the most favorable pathway is clarified. The difference between the mechanism of the methyl migration and that of the chlorine migration can be ascribed to the presence of a low-lying pair of electrons in the migrating species in the latter case.

It is interesting to examine the intramolecular acid-catalyzed isomerization of allyl alcohols[14] in relation to the chlorine migration described above.



In this case, the transfer of the double-bond and the migration of the hydroxyl group as a neutral water molecule are supposed to take place simultaneously.[14b] It is considered that the path of isomerization may be similar to the chlorine migration, water molecule being bonded to two terminal carbons of the allylic framework at the transition state, because the migrating species has a lone pair orbital relevant to the orbital interaction with the π_1 and π_3 MO's and another lone pair orbital to the interaction with π_2 MO of the allyl fragment.

Conclusion

It is concluded here that 1,3-sigmatropic rearrangement may occur suprafacially on the allylic framework with retention of the configuration of the migrating center as the result of a successive 1,2-shift with a radical nature. This is interpreted by the SOMO-SOMO interaction between the allyl radical and the methyl radical in the initial stage and the subsidiary orbital effect near the transition state. In the chlorine migration the HOMO-LUMO interaction between the allyl cation and the chloride anion provides the dominant stabilization to the reaction system. From the present calculation, it is clarified that the mechanism of 1,3-migration in allylic framework depends on the property of the migrating species.

We would like to express our gratitude to the Data Processing Center, Kyoto University, for its generous permission to use the FACOM 230-75 computer. Our MO calculation was carried out under the financial support of the Ministry of Education (Grant-in-Aid 047068).

References

1) (a) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin and B. Pullmann, Ed., Academic Press, New York, N. Y. (1964), p. 513; (b) K. Fukui and H. Fujimoto, "Mechanisms of Molecular Migration," ed by B. S. Thyagarajan, Interscience, Vol. 2, New York, N. Y. (1969), p. 118; (c) K. Fukui, "Theory of Orientation and Stereoselection," Springer-Verlag, Heidelberg (1970).

2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y. (1970).

3) (a) J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, **94**, 8917 (1972); (b) J. A. Berson, *Acc. Chem. Res.*, **5**, 406 (1972); (c) S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **97**, 6108 (1975); (d) N. D. Epiotis, *ibid.*, **94**, 1924 (1972); (e) K. Yamaguchi, T. Fueno, and H. Fukutome, *Chem. Phys. Lett.*, **22**, 461 (1973); (f) W. Schmidt, *Tetrahedron Lett.*, **1972**, 581.

4) (a) J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **92**, 1096 (1970); (b) J. A. Berson and P. B. Dervan, *ibid.*, **95**, 269 (1973); (c) J. A. Berson and R. W. Holder, *ibid.*, **95**, 2073 (1973); (d) J. A. Berson, T. Miyashi, and G. Jones, II, *ibid.*, **96**, 3468 (1974); (e) J. Meinwald and D. Schmidt, *ibid.*, **91**, 5877 (1969); (f) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969); (g) R. C. Cookson and J. E. Kemp, *Chem. Commun.*, **1971**, 385.

5) W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951).

6) (a) H. M. Niemeyer and P. Ahlberg, *Chem. Commun.*, **1974**, 799; (b) H. M. Niemeyer, O. Goscinski, and P. Ahlberg, *Tetrahedron*, **31**, 1699 (1975); (c) F. Bernardi, N. D. Epiotis, and R. L. Yates, *J. Am. Chem. Soc.*, **97**, 1334 (1975); (d) N. D. Epiotis, R. L. Yates, and F. Bernardi, *ibid.*, **97**, 4198 (1974).

7) (a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y. (1970); (b) P. E. Stevenson and D. L. Burkey, *J. Am. Chem. Soc.*, **96**, 3061 (1974).

8) C. Edmiston and K. Reudenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

9) D. A. Dixon and W. N. Lipscomb, *J. Am. Chem. Soc.*, **95**, 2854 (1973).

10) We shall examine the interaction of the carbon p orbital having one electron with the occupied π_1 orbital and the unoccupied π_3 orbital. This interaction gives three orbitals. The lowest energy level orbital given by the interaction is depressed relative to the π_1 by the interaction between the p and π_1. The new radical orbital energy level is not remarkably affected, because the interaction between the p and π_1 raises the new radical orbital but that between the p and π_3 depresses the radical orbital. Thus the transition state is considered to be stabilized. Similar discussion is implicitly included in Ref. 3a.

11) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971).

12) The rate ratio of the suprafacial 1,3-sigmatropic rearrangement with retention to that with inversion was observed to be greater on *endo*-7-*exo*-methylbicyclo[3.2.0]heptenyl acetate than on *endo*-7-*exo*-D-bicyclo[3.2.0]heptenyl acetate.[4c] This observation seems to show that the migrating group with an electron donating group would make the 1,3-rearrangement occur easily since the methyl group is considered to be an electron donating one.

13) The high stereospecificity was observed in the case of bisallyl system.[4d,4e,4f] In this case there is another factor, a multi-cyclic interaction. *C.f.*, S. Inagaki, T. Minato, H. Fujimoto, and K. Fukui, *Chem. Lett.*, **1976**, 89.

14) (a) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," ed by S. Patai, Interscience, New York (1964), Chap. 10; (b) E. A. Braude and E. R. Jones, *J. Chem. Soc.*, **1944**, 436; (c) W. G. Young, K. Nozaki, and R. Warner, *J. Am. Chem. Soc.*, **61**, 2564 (1939); (d) H. L. Georing and R. R. Josephson, *ibid.*, **84**, 2779 (1962).