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# An MO-Theoretical Study of the E2 Reaction of Ethyl Chloride

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The change in the electronic state in the course of the E2 reaction of ethyl chloride was followed by means of the extended Hückel calculation. A model is adopted in which the nucleophilic reagent approaches the *trans*-$\beta$-hydrogen atom. The valence-inactive population of the *trans*-$\beta$-hydrogen atom in the lowest unoccupied (LU) molecular orbital (MO) was employed as a theoretical reactivity index. The theoretical conclusion derived was consistent with the experimental results.

The mechanism of the base-promoted, bimolecular elimination (E2) reactions has been experimentally studied in detail.[1] In this type of reaction, the attack of bases on the $\beta$-hydrogen atom and the departure of the nucleophile, X, from the $\alpha$-carbon atom are thought to occur in concert with the double-bond formation between the $C_\alpha$–$C_\beta$ bond, and it is accepted that the hydrogen atom *trans* coplanar with respect to the leaving group is

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[1] See, *e.g.*, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York (1953), p. 419.

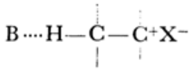
attacked dominantly.

In one of our previous papers[2)] we, using MO calculations, have shown that the base should attack the *trans-β*-hydrogen atom most easily. Also, a quantitative method to interpret the reactivity in E2 reactions has been proposed.[3)]

In the present paper, the change in the electronic state in the course of the E2 reaction of ethyl chloride will be discussed by the use of the extended Hückel method proposed by Hoffmann.[4)] It is well established that this MO method is suitable for treating the electronic structure of sizable molecules which include unstable intermediates. Indeed, the mechanisms of various kinds of organic reactions have already been elucidated by means of this method.[2,3,5–10)]

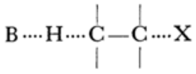
## Setting-up of the Reaction Model

The *β*-eliminations are said to proceed by means of the following three processes[1)]: one is the usual E2 mechanism (II), and the others are the two-step mechanisms, E1 (I) and E1cB (III).



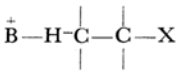
$B\cdots H-C-C^{+}X^{-}$

(I)



$B\cdots H\cdots C-C\cdots X$

(II)



$\overset{+}{B}-H^{-}C-C-X$

(III)

Various examples of E1 reactions are known, while the carbanion mechanism (E1cB) is observed only in the extreme case where the *β*-carbon atom bears strongly-electron-attracting substituents.[11)] It is considered that a bimolecular E2 reaction proceeds through a transition state like the II type, with varying contributions of I and III, depending on the structure and the reaction conditions.[12–14)]

An alternative E2 mechanism in which $S_N2$ and E2 are "merged"[15,16)] has been proposed, but it applies only to very special cases.[17)]

In view of this, it is appropriate to adopt the model for the bimolecular elimination in the staggered ethyl chloride molecule as occurring in normal E2 fashion, with a concerted and a nearly complete synchronous mechanism.

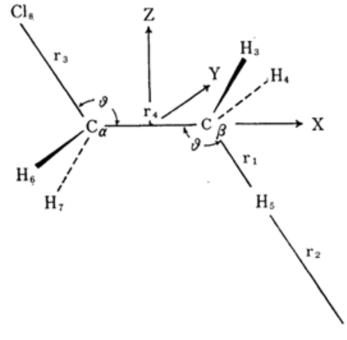


Fig. 1. The coordinates for the reacting system.

TABLE 1. THE ASSUMED GEOMETRIES OF REACTING SYSTEM

| Model No. | $\vartheta$ (°) | $r_1$ (Å) | $r_2$ (Å) | $r_3$ (Å) | $r_4$ (Å) |
|---|---|---|---|---|---|
| Ethyl chloride | * | 1.09 | | 1.77 | 1.54 |
| I | 109 | 1.09 | 3.00 | 1.78 | 1.54 |
| II | 108 | 1.11 | 2.70 | 1.81 | 1.54 |
| III | 107 | 1.13 | 2.40 | 1.84 | 1.54 |
| IV | 106 | 1.15 | 2.20 | 1.87 | 1.54 |
| V | 105 | 1.17 | 2.00 | 1.91 | 1.54 |
| V-1 | 105 | 1.17 | 2.00 | 1.91 | 1.51 |
| V-2 | 105 | 1.17 | 2.00 | 1.91 | 1.48 |
| V-3 | 105 | 1.17 | 2.00 | 1.91 | 1.45 |
| V-4 | 105 | 1.17 | 2.00 | 1.91 | 1.42 |
| VI | 100 | 1.36 | 1.75 | 2.05 | 1.54 |
| VI′ | 100 | 1.36 | 1.75 | 2.05 | 1.51 |
| VII | 95 | 2.00 | 1.50 | 2.70 | 1.54 |
| VII′ | 95 | 2.00 | 1.50 | 2.70 | 1.51 |
| Ethylene | 90 | 1.09 | | | 1.34 |

* $\angle CCCl = 110°$, $\angle CCH = 109.5°$

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2) K. Fukui and H. Fujimoto, *Tetrahedron Letters*, **1965**, 4303.

3) K. Fukui, H. Hao and H. Fujimoto, This Bulletin, **42**, 348 (1969).

4) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964).

5) H. Kato, T. Yonezawa, K. Morokuma and K. Fukui, This Bulletin, **37**, 1710 (1964).

6) H. Kato, K. Yamaguchi, T. Yonezawa and K. Fukui, *ibid.*, **38**, 2144 (1965).

7) T. Yonezawa, O. Yamamoto, H. Kato and K. Fukui, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 26 (1966).

8) H. Fujimoto and K. Fukui, *Tetrahedron Letters*, **1966**, 5551.

9) T. Yonezawa, H. Konishi, H. Kato, K. Morokuma and K. Fukui, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **69**, 869 (1966).

10) T. Yonezawa, K. Shimizu and H. Kato, This Bulletin, **40**, 456, 1302 (1967).

11) J. Hine, R. Wiesböck and O. B. Ramsay, *J. Am. Chem. Soc.*, **83**, 1222 (1961); T. I. Crowell, A. A. Wall, R. T. Kemp and R. E. Lutz, *ibid.*, **85**, 2521 (1963).

12) J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962); *Angew. Chem., Intern. Ed. Engl.* **1**, 225 (1962).

13) R. F. Hudson, J. Arendt and A. Mancuso, *J. Chem. Soc.* (*B*), **1967**, 1069.

14) L. J. Steffa and E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 6149 (1967).

15) G. M. Fraser and H. M. R. Hoffmann, *J. Chem. Soc.* (*B*), **1967**, 425.

16) A. J. Parker, M. Ruane, G. Biale and S. Winstein, *Tetrahedron Letters*, **1968**, 2113.

17) Compare the claims of, *e.g.*, J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, **32**, 11 (1967), and D. J. McLennan, *J. Chem. Soc.* (*B*), **1966**, 705.

For the convenience of calculation, we employ a chloride anion as the attacking base. The coordinates of this reacting system are presented in Fig. 1, where $Cl_8$, $C_\alpha$, $C_\beta$, $H_5$, and $Cl_9$ atoms lie in the X–Z plane, the line of $C_\alpha$–$C_\beta$ being taken as the X-axis. The origin of the coordinates is at the middle point between $C_\alpha$ and $C_\beta$. The angles, $H_5$–$C_\beta$–$H_4$, $H_5$–$C_\beta$–$H_3$, $H_5$–$C_\beta$–$C_\alpha$, $Cl_8$–$C_\alpha$–$H_6$, $Cl_8$–$C_\alpha$–$H_7$, and $Cl_8$–$C_\alpha$–$C_\beta$, are all assumed to be equal to $\vartheta$, and $r_1$, $r_2$, and $r_3$ refer to the distances of $C_\beta$–$H_5$, $H_5$–$Cl_9$, and $C_\alpha$–$Cl_8$ respectively.

Here, we set up various combinations of $r_1$, $r_2$, $r_3$, and $\vartheta$, as shown in Table 1. In these models, all the $C_\alpha$–$C_\beta$ and C–H bond distances, except for $C_\beta$–$H_5$, are fixed at 1.54 Å and 1.09 Å respectively. Of course, the $C_\alpha$–$C_\beta$ distance will vary with the reaction path. Therefore, in order to cover this ambiguity, we have changed the $C_\alpha$–$C_\beta$ $(=r_4)$ distance in the models from V-1 to V-4 and in the models VI′ and VII′, as is shown in Table 1.

## Method of Calculation

The numerical values used in the extended Hückel calculation are the same as those in the preceding paper.[3] For the sake of simplicity, the Coulomb integral of the attacking chloride anion is assumed to be constant throughout, equal to that of the neutral atom. The various populations calculated are defined as indicated in Table 2,[18]

TABLE 2. DEFINITION OF VARIOUS POPULATIONS

The AO population of AO $r$;

$$N(r) = 2\sum_{j}^{\text{occ}}\sum_{s} C_r^j C_s^j S_{rs}$$

The valence-inactive AO population of AO $r$;

$$p(r) = 2\sum_{j}^{\text{occ}}(C_r^j)^2$$

The valence-active AO population of AO $r$;

$$v(r) = 2\sum_{j}^{\text{occ}}\sum_{s\neq r} C_r^j C_s^j S_{rs}$$

The atom population of atom A;

$$M(\mathrm{A}) = \sum_{r}^{\mathrm{A}} N(r)$$

The AO bond population between AO's $r$ and $s$;

$$N(r\text{–}s) = 4\sum_{j}^{\text{occ}} C_r^j C_s^j S_{rs}$$

The atom bond population between atoms A and B;

$$M(\mathrm{A\text{–}B}) = \sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}} N(r-s)$$

where $r$ and $s$ denote the $r$th and $s$th atomic orbitals respectively; $C_r^j$ is the coefficient of the $r$th atomic orbital in the $j$th molecular orbital; $\sum_j^{\text{occ}}$ refers to the summation over all the occupied orbitals; $\sum_r^{\mathrm{A}}$ signifies the sum over all the atomic orbitals belonging to the atom, A, and $S_{rs}$ is the overlap integral between the $r$th and $s$th atomic orbitals as calculated by Mulliken's formula with Slater-type AO's.[19]

The geometry of an isolated ethyl chloride molecule is determined by the following interatomic distances and bond angles:[20]

C–Cl 1.77Å, C–C 1.54Å, C–H 1.09Å, ∠ClCC 110°

Also, the shape of ethylene molecule is taken as follows:

C–C 1.34Å, C–H 1.09Å, all angles 120°

## Results and Discussions

### 1. The Electronic Structure of Ethyl Chloride.

**1. The Electronic Structure of Ethyl Chloride.** The highest occupied (HO) MO and the lowest unoccupied (LU) MO of ethyl chloride and their energies are shown in Table 3. The obtained HO energy, −12.5864 eV, is somewhat lower than is to be expected from the ionization potential value, 10.97 eV, or from the value, 11.2

TABLE 3. THE AO COEFFICIENTS AND ENERGY OF HO AND LU MO's OF ETHYL CHLORIDE

| | HO | LU |
|---|---|---|
| Orbital energy, eV | −12.5864 | 1.3394 |
| $S_{C_\alpha}$* | 0 | 0.140 |
| $X_{C_\alpha}$ | 0 | −0.592 |
| $Y_{C_\alpha}$ | −0.343 | 0 |
| $Z_{C_\alpha}$ | 0 | 0.911 |
| $S_{C_\beta}$ | 0 | 0.056 |
| $X_{C_\beta}$ | 0 | −0.406 |
| $Y_{C_\beta}$ | 0.133 | 0 |
| $Z_{C_\beta}$ | 0 | 0.069 |
| $H_3$ | −0.117 | −0.004 |
| $H_4$ | 0.117 | −0.004 |
| $H_5$ | 0 | 0.281 |
| $H_6$ | 0.258 | 0.099 |
| $H_7$ | −0.258 | 0.099 |
| $S_{Cl_8}$ | 0 | −0.542 |
| $X_{Cl_8}$ | 0 | −0.224 |
| $Y_{Cl_8}$ | 0.867 | 0 |
| $Z_{Cl_8}$ | 0 | 0.706 |

* The symbols $S_C$, $X_C$, $Y_C$ and $Z_C$ refer to the 2s, 2px, 2py and 2pz orbitals of the carbon atom and $H_i$ denotes the 1s orbital of the $i$th hydrogen atom. The $S_{Cl}$, $X_{Cl}$, $Y_{Cl}$ and $Z_{Cl}$ signify the 3s, 3px, 3py and 3pz orbitals of the chlorine atom.

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18) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841, 2338, 2343 (1955).

19) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *ibid.*, **17**, 1248 (1949).

20) J. Y. Beach and D. P. Stevenson, *J. Am. Chem. Soc.*, **61**, 2463 (1939).

eV reported by Irsa$^{21)}$ and Watanabe.$^{22)}$ The energy of LU MO, 1.3394 eV, is considerably lower than the value, 3.2120 eV, of ethane,$^{23)}$ reflecting the reactivity toward the nucleophilic attack. The HO level shows a $\pi$-type character, with the direction of extension parallel to the Y-axis; the occupying electrons are largely localized on the Cl 3py and $C_\alpha$ 2py orbitals, thus contributing to the C–H bonding. The LU orbital is of a p$\sigma$-type, with a strong antibonding character on the $C_\alpha$–Cl and $C_\alpha$–$C_\beta$, especially on the former. These trends correspond to the fact that the $C_\alpha$–Cl bond is weakened by the electron transfer from the approaching nucleophilic reagent. In this MO the coefficient of the $\beta$-hydrogen atom ($H_5$) situated *trans* to the chlorine atom is the largest among those of the hydrogen orbitals, as has already been pointed out.$^{2)}$

### 2. The Change in the Electronic Structure of Ethyl Chloride along the Reaction Path.

*2-1. The Change in AO Populations.* It is, of course, not confirmed that the models adopted, indicated in Table 1, correspond to the points on the reaction path on the potential energy surface. However, they at least provide us with some qualitative information concerning the electronic process of the reaction.

The calculated values of the total energy in models I—VII are given in Table 4. The results show that the total energy increases as the reaction proceeds reaching a maximum in model VI.

The atom population, $M$(A), in each atom is also shown in Table 4. The $M(C_\beta)$ increases from 4.387 at the initial state (ethyl chloride) to 4.705 in model VI, and then it decreases. On the contrary, $M(C_\alpha)$ decreases from 3.958 to 3.862 in model VI and then increases to 4.234 at the final product (ethylene) through the model VII, 4.079. From these data, $C_\alpha$ and $C_\beta$ seem to form, respectively, the cationic and anionic centers in the transition state; afterwards, however, they approach electronically the same state. The $\beta$-hydrogen atom ($H_5$) is attacked by the base, which possesses monotonously decreasing values of $M(H_5)$, while the atom population of the leaving nucleophilic chlorine atom, $M(Cl_8)$, increases from 7.260 to 7.926. Hence, we find that the $H_5$ and $Cl_8$ atoms are likely to depart from the molecule as a cation and an anion respectively; this is consistent with the experimental results. It should be noted that the $M$(H) values of the hydrogen atoms which have less direct concern with the reaction, *i.e.*, $H_3(=H_4)$ and $H_6(=H_7)$, are almost unchanged.

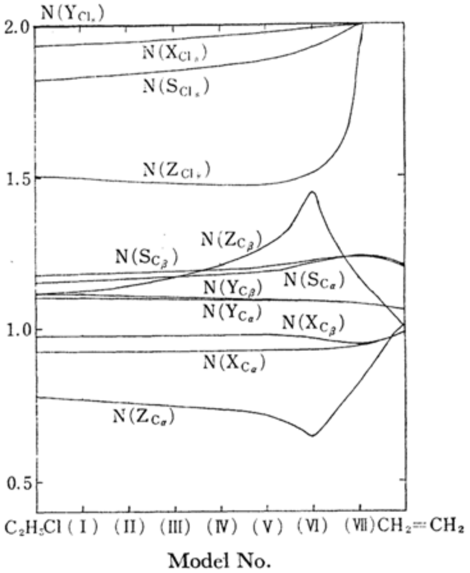

Fig. 2. The change of AO populations, $N(r)$, of the $C_\alpha$, $C_\beta$ and $Cl_8$ atoms in the reaction processes.

In order to obtain further knowledge, the AO populations of various atoms are collected in Fig. 2. The $N(Zc_\beta)$ increases remarkably from 1.114 at

TABLE 4. THE CALCULATED VALUES OF THE TOTAL ENERGY (eV) $E$, AND THE ATOM POPULATION, $M$(A), OF EACH ATOM IN ETHYL CHLORIDE, MODEL I—VII, AND ETHYLENE

| | $E$ | $M(C_\beta)$ | $M(C_\alpha)$ | $M(Cl_8)$ | $M(Cl_9)$ | $M(H_5)$ | $M(H_3)$ | $M(H_6)$ |
|---|---|---|---|---|---|---|---|---|
| $C_2H_5Cl$ | | 4.387 | 3.958 | 7.260 | | 0.874 | 0.875 | 0.886 |
| I | −474.8297 | 4.397 | 3.955 | 7.264 | 7.994 | 0.870 | 0.874 | 0.886 |
| II | −474.8893 | 4.405 | 3.945 | 7.277 | 7.985 | 0.868 | 0.875 | 0.886 |
| III | −474.8199 | 4.435 | 3.935 | 7.290 | 7.964 | 0.857 | 0.874 | 0.886 |
| IV | −474.6652 | 4.476 | 3.925 | 7.304 | 7.938 | 0.840 | 0.874 | 0.885 |
| V | −474.3657 | 4.545 | 3.912 | 7.324 | 7.896 | 0.810 | 0.872 | 0.884 |
| VI | −473.9012 | 4.705 | 3.862 | 7.415 | 7.754 | 0.762 | 0.870 | 0.881 |
| VII | −475.6913 | 4.416 | 4.079 | 7.926 | 7.388 | 0.697 | 0.872 | 0.875 |
| $CH_2$=$CH_2$ | | 4.234 | 4.234 | | | | 0.883 | 0.883 |

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21) A. P. Irsa, *J. Chem. Phys.*, **26**, 18 (1957).

22) K. Watanabe, *ibid.*, **26**, 542 (1957).

23) Kagaku Zokan, **26**, "Yuki Ryoshi Kagaku," Kagaku Dozin, Kyoto (1966), p. 257.

the ethyl chloride to 1.446 at model VI and is responsible for making $C_\beta$ an anionic center, while the $N(Zc_\alpha)$ decreases prominently from 0.776 to 0.649, thus mainly contributing to the cationic character of the $C_\alpha$ atom in model VI. We can also see that the electrons gradually migrate from the $\beta$-carbon 2px orbital to the $\alpha$-carbon 2s orbital, and from the 2py orbitals of both carbon atoms to the $H_3$, $H_4$, $H_6$, and $H_7$ atoms. The AO populations of the 2s orbitals of both carbon atoms, $N(Sc_\alpha)$ and $N(Sc_\beta)$, increase monotonously. This may correspond to the carbon hybridization change from $sp^3$ to $sp^2$, in which the valence electrons in the $C_\alpha$–$Cl_8$ and $C_\beta$–$H_5$ bonds become localized at the 2s orbitals as the $Cl_8$ and $H_5$ atoms start to leave both the carbon atoms.

The changes in the AO populations of $Cl_8$ were found to decrease in the order of $N(Z_{Cl_8}) > N(S_{Cl_8}) > N(X_{Cl_8})$. The $N(Y_{Cl_8})$ is almost constant, *ca.* 2.000. Therefore, the 2py orbital of the $Cl_8$ atom is assigned to a lone-pair orbital.

*2-2. The Change in Bond Populations.* The atom bond population, $M(C_\alpha–C_\beta)$, increases from 0.700 (ethyl chloride) to 1.024 (Model VII), as is shown in Fig. 3.

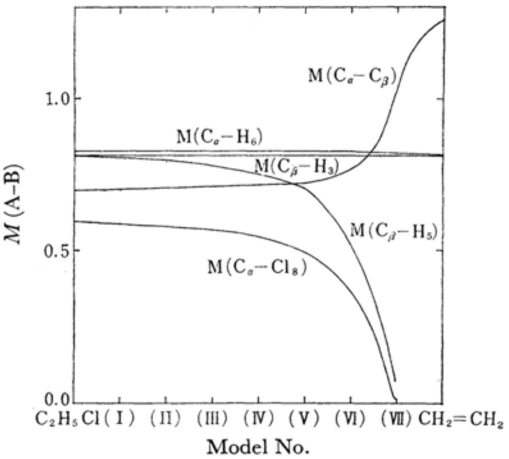

Fig. 3. The change of the atom bond populations, $M$ (A–B), in the various models.

The values of $M(C_\alpha–Cl_8)$ and $M(C_\beta–H_5)$ decrease as their bond distances increase. The $M(C_\beta–H_3)$ and $M(C_\alpha–H_6)$ remain almost unchanged.

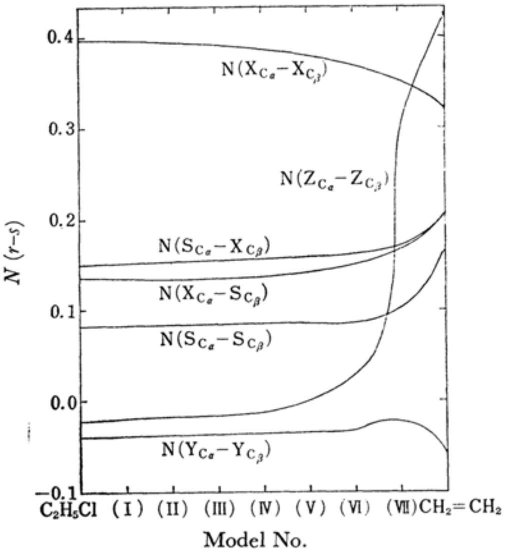

Fig. 4. The change of AO bond populations between $\alpha$- and $\beta$-carbons.

For a further discussion of the C–C bond, the AO bond populations are listed in Fig. 4. The $N(Zc_\alpha–Zc_\beta)$ increases most remarkably from $-0.022$ to 0.285 (Model VII), contributing dominantly to the increase in $M(C_\alpha–C_\beta)$. Obviously, this reflects the progress of the double-bond formation. In models I—V, $N(Zc_\alpha–Zc_\beta)$ exhibits an antibonding nature, whereas models VI and VII indicate a bonding between the two 2pz orbitals. The $N(Xc_\alpha–Xc_\beta)$ and $N(Yc_\alpha–Yc_\beta)$ are larger than ethylene throughout the models from I to VII.

*2-3. Influence of the Change in C–C Bond Distance upon the Electronic Structure.* In the discussion above, the C–C bond distance was tentatively fixed as equal to 1.54Å. Now let us investigate the influence of the change in C–C bond distance.

Let us vary the $C_\alpha$–$C_\beta$ bond distance in model V as is shown in Table 1. The mode of the change in the electronic structure is given in Table 5 and in Figs. 5—7. These transient models seem to fit the states before the transition state, since the total energies are lower than the tentatively-assumed model VI. With the change from V to V-4, $M(C_\alpha)$ and $M(C_\beta)$ are reduced, showing an electron shift from the $\alpha$-carbon to $Cl_8$, $H_6$, and $H_7$ and from the $\beta$-carbon to $H_3$ and $H_4$, while $M(H_5)$ and

TABLE 5. THE CALCULATED VALUES OF THE TOTAL ENERGY (eV), $E$, AND ATOM POPULATION $M$(A) IN MODELS V-1—V-4

| | $E$ | $M(C_\beta)$ | $M(C_\alpha)$ | $M(Cl_8)$ | $M(Cl_9)$ | $M(H_5)$ | $M(H_3)$ | $M(H_6)$ |
|---|---|---|---|---|---|---|---|---|
| V-1 | −474.7471 | 4.546 | 3.895 | 7.333 | 7.888 | 0.809 | 0.875 | 0.890 |
| V-2 | −474.5721 | 4.542 | 3.891 | 7.338 | 7.887 | 0.809 | 0.876 | 0.891 |
| V-3 | −474.3768 | 4.537 | 3.889 | 7.344 | 7.887 | 0.809 | 0.877 | 0.892 |
| V-4 | −474.1588 | 4.533 | 3.883 | 7.349 | 7.886 | 0.809 | 0.878 | 0.893 |

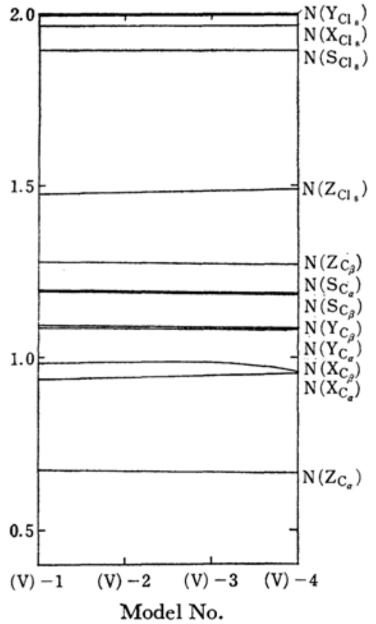

Fig. 5. The change of AO populations, $N(r)$, in the models V-1—V-4.

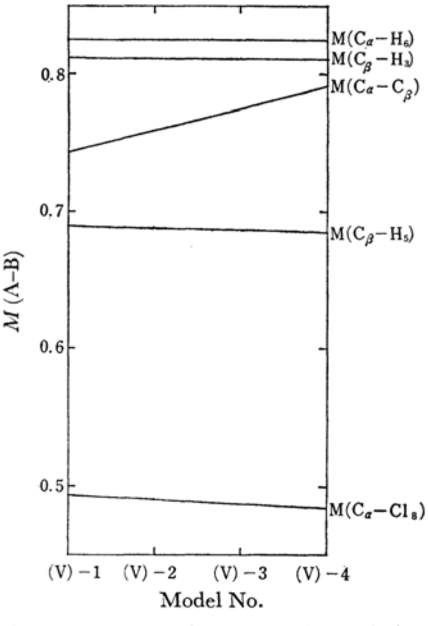

Fig. 6. The change of atom bond populations in the models V-1—V-4.

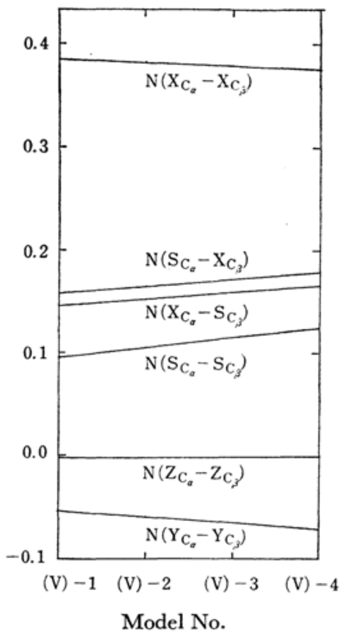

Fig. 7. The change of AO bond populations between α- and β-carbons in the models V-1—V-4.

$M(Cl_9)$ remain almost unchanged. The changes in AO populations are listed in Fig. 5. The data indicate that $N(Sc_\alpha)$ and $N(Sc_\beta)$ decrease, while $N(Xc_\alpha)$ and $N(Xc_\beta)$ increase.

Figure 6 shows that $M(C_\beta\text{–}H_3)$ and $M(C_\alpha\text{–}H_6)$ remain constant. The $M(C_\beta\text{–}C_3)$ increases with a decrease in the $C_\alpha$–$C_\beta$ bond distance, while $M(C_\alpha\text{–}Cl_8)$ and $M(C_\beta\text{–}H_5)$ change in the reverse fashion. The AO bond populations, $N(Sc_\alpha\text{–}Xc_\beta)$ and $N(Xc_\alpha\text{–}Sc_\beta)$ increase from 0.157 to 0.179 and from 0.142 to 0.166 respectively, as may be seen in Fig. 7. In this step of the reaction, the double-bond formation is not yet appreciable, as may be understood from the negative values of $N(Zc_\alpha\text{–}Zc_\beta)$.

Next, let us investigate the effect of the $C_\alpha$–$C_\beta$ bond distance near and after the transition state. Among the models listed in Table 1, models VI and VII seem to correspond to such states. If we change the bond distance from 1.54Å to 1.51Å, $M(C_\beta)$ decreases from 4.416 to 4.397, while $M(C_\alpha)$ increases from 4.079 to 4.090, in model VII, as may be observed from Tables 4 and 6. In this electron migration, the 2pz orbitals play a dominant role. The increase in $N(Zc_\alpha\text{–}Zc_\beta)$ expresses the double-bond formation. All the other populations, $N(r)$, $M(A)$, $N(r\text{–}s)$, and $M(A\text{–}B)$, in models VI′ and VII′, except for $M(C_\alpha)$ and $N(Zc_\alpha)$ in model VI′, come close to the corresponding ones of the ethylene molecule.

*2-4. The Change in the Electronic Structure of the Leaving Chlorine Atom.* In Section 2-1, it has been noted that the $Cl_8$ 2py AO exhibits a lone-pair-like behavior. In this connection let us now attempt to discuss this point in more detail by the use of the concept of the valence atomic orbital (VAO) proposed by Ruedenberg.[24] The VAO is the orbital which makes the diagonal elements of the intra-atomic local bond order matrix reach a maximum

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[24] K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 356 (1962).

TABLE 6. THE CALCULATED VALUES OF THE TOTAL ENERGY (eV) $E$, AND THE VARIOUS POPULATIONS IN MODEL VI′ AND VII′

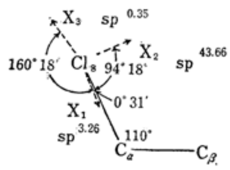
| | $E$ | $M(C_\beta)$ | $M(C_\alpha)$ | $M(Cl_8)$ | $M(Cl_9)$ | $M(H_5)$ | $M(H_3)$ | $M(H_6)$ |
|---|---|---|---|---|---|---|---|---|
| VI′ | −474.7928 | 4.697 | 3.859 | 7.425 | 7.753 | 0.760 | 0.871 | 0.882 |
| VII′ | −475.9340 | 4.397 | 4.090 | 7.928 | 7.385 | 0.698 | 0.874 | 0.878 |

| | $N(S_{C_\beta})$ | $N(X_{C_\beta})$ | $N(Y_{C_\beta})$ | $N(Z_{C_\beta})$ | $N(S_{C_\alpha})$ | $N(X_{C_\alpha})$ | $N(Y_{C_\alpha})$ | $N(Z_{C_\alpha})$ | $N(S_{Cl_8})$ | $N(X_{Cl_8})$ | $N(Y_{Cl_8})$ | $N(Z_{Cl_8})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| VI′ | 1.210 | 0.969 | 1.079 | 1.439 | 1.202 | 0.931 | 1.078 | 0.648 | 1.925 | 1.989 | 2.000 | 1.511 |
| VII′ | 1.229 | 0.949 | 1.070 | 1.149 | 1.235 | 0.947 | 1.070 | 0.837 | 1.997 | 1.999 | 2.000 | 1.932 |

| | $M(C_\beta\text{–}H_3)$ | $M(C_\alpha\text{–}H_6)$ | $M(C_\alpha\text{–}C_\beta)$ | $M(C_\alpha\text{–}Cl_8)$ | $M(C_\beta\text{–}H_5)$ |
|---|---|---|---|---|---|
| VI′ | 0.815 | 0.830 | 0.792 | 0.376 | 0.511 |
| VII′ | 0.817 | 0.820 | 1.056 | 0.021 | 0.081 |

| | $N(S_{C_\alpha}\text{–}S_{C_\beta})$ | $N(X_{C_\alpha}\text{–}X_{C_\beta})$ | $N(Y_{C_\alpha}\text{–}Y_{C_\beta})$ | $N(Z_{C_\alpha}\text{–}Z_{C_\beta})$ | $N(X_{C_\alpha}\text{–}S_{C_\beta})$ | $N(S_{C_\alpha}\text{–}X_{C_\beta})$ |
|---|---|---|---|---|---|---|
| VI′ | 0.100 | 0.365 | −0.035 | 0.034 | 0.158 | 0.170 |
| VII′ | 0.101 | 0.351 | −0.034 | 0.301 | 0.167 | 0.169 |

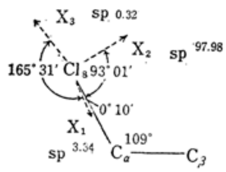
$C_2H_5Cl$



$X_1=0.485S+0.292X-0.825Z$
$X_2=0.150S+0.901X+0.407Z$
$X_3=0.862S-0.320X+0.393Z$

| $p(X_1)$ | $p(X_2)$ | $p(X_3)$ |
|---|---|---|
| 0.999 | 2.022 | 2.029 |

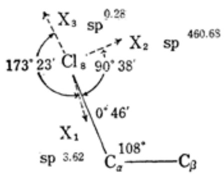
I



$X_1=0.480S+0.283X-0.830Z$
$X_2=0.096S+0.883X+0.357Z$
$X_3=0.871S-0.271X+0.410Z$

| $p(X_1)$ | $p(X_2)$ | $p(X_3)$ |
|---|---|---|
| 1.004 | 2.022 | 2.029 |

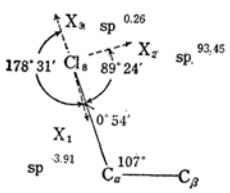
II



$X_1=0.465S+0.262X-0.845Z$
$X_2=0.047S+0.947X+0.319Z$
$X_3=0.884S-0.188X+0.428Z$

| $p(X_1)$ | $p(X_2)$ | $p(X_3)$ |
|---|---|---|
| 1.026 | 2.022 | 2.030 |

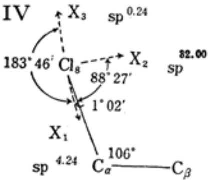
III



$X_1=0.451S+0.248X-0.857Z$
$X_2=0.010S+0.959X+0.282Z$
$X_3=0.892S-0.136X+0.430Z$

| $p(X_1)$ | $p(X_2)$ | $p(X_3)$ |
|---|---|---|
| 1.048 | 2.022 | 2.031 |

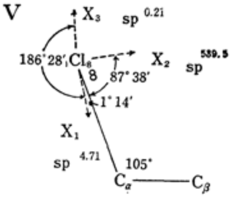
IV



$X_1=0{,}437S+0.232X-0.869Z$
$X_2=-0.019S+0.968X+0.249Z$
$X_3=0.899S-0.093X+0.427Z$

| $p(X_1)$ | $p(X_2)$ | $p(X_3)$ |
|---|---|---|
| 1.072 | 2.021 | 2.032 |

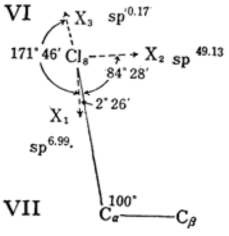
V



$X_1=0.418S+0.216X-0.882Z$
$X_2=-0.043S+0.975X+0.218Z$
$X_3=0.907S-0.053X+0.417Z$

| $p(X_1)$ | $p(X_2)$ | $p(X_3)$ |
|---|---|---|
| 1.106 | 2.019 | 2.033 |

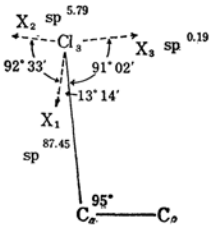
VI



$X_1=0.354S+0.123X-0.927Z$
$X_2=-0.141S+0.987X+0.077Z$
$X_3=0.925S-0.104X+0.366Z$

| $p(X_1)$ | $p(X_2)$ | $p(X_3)$ |
|---|---|---|
| 1.255 | 2.015 | 2.034 |

VII



$X_1=0.106S-0.142X-0.984Z$
$X_2=0.384S-0.907X+0.173Z$
$X_3=0.917S+0.396X+0.042Z$

| $p(X_1)$ | $p(X_2)$ | $p(X_3)$ |
|---|---|---|
| 1.928 | 2.001 | 2.011 |

Fig. 8. The VAO $X_r$, valence-inactive populations $p(X_r)$, hybrid states and bond angles of $Cl_8$ in the reaction processes.

or a minimum. The four VAO's belonging to the leaving chlorine atom attached to the $\alpha$-carbon atom are designated as X, $X_2$, $X_3$, and $X_4$, among which $X_4$ is taken to be associated with the 3py orbital. These VAO's are obtained by using the bond-order matrix obtained by the extended Hückel calculation. The results are shown along with the hybrid states and the valence-inactive populations, in Fig. 8. The VAO $X_1$ is supposed to be associated with the $Cl_8$–$C_\alpha$ bond. The calculated valence angles of $X_1$ are well in agreement with the assumed angle, $\angle Cl_8C_\alpha C_\beta$, in models I—VI. (In Fig. 8, the discrepancy from the $Cl_8$–$C_\alpha$ bond is shown.) The hybrid of $X_1$ changes from $sp^{3.34}$ at the model I to $sp^{87.5}$ at the model VII. This indicates that $X_1$ becomes a 3p lone-pair orbital as the reaction proceeds. The $X_2$ and $X_3$ orbitals are lone-pair orbitals mainly composed of 3p and 3s AO respectively. As the reaction proceeds, the discrepancy of the obtained bond angle from the assumed angle becomes greater; *e.g.*, it is 13°14′ in model VII. This seems to be due to the decrease in the valence-active population between $C_\alpha$ and $Cl_8$ atoms.

The calculations were carried out on the HITAC 5020 computer at the computation center of the University of Tokyo.