A Molecular Orbitals Study of the Nucleophilic Substitution in Methyl Chloride

By Hiroshi KATO, Keiji MOROKUMA, Teijiro YONEZAWA and Kenichi FUKUI

(Received April 9, 1965)

The mechanism of the S_N2-type nucleophilic substitution of aliphatic compounds has been discussed in many experimental studies.[1] Some quantitative and semi-quantitative interpretations of this type of reaction have been carried out by using semi-empirical theory[2,3] or by means of a simple LCAO-MO method.[4] No attempt, however, has yet been made to throw light on the mechanism of the electronic process of this type of reaction. Recently Hoffmann has proposed an extended Hückel method in which an MO (molecular orbital) is represented by linear combination of valence AO's (atomic orbitals) in the molecule.[5] As will be shown in the next section, this procedure, along with the Born-Oppenheimer adiabatic approximation, is particularly convenient and effective for treating the electronic structure of unstable intermediates or such molecules as contain atoms with an unusual valency, as well as ordinary stable molecules.

Accordingly, in the present paper we intend to apply this method to a discussion of the electronic structure of the molecular system which would appear near the transition state of the typical S_N2-type reaction, $CH_3Cl+Cl^- \rightarrow Cl^- +CH_3Cl$. This species may be written schematically as $(Cl\cdots CH_3\cdots Cl)^-$.

The calculated results will help us to ascertain the characteristic role which might be

---

[1] E. g., C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y. (1953).

[2] P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. D. H. Mackie, *J. Chem. Soc.*, **1955**, 3200; I. Dostrovsky, E. D. Hughes and C. K. Ingold, ibid., **1946**, 173.

[3] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Process," McGraw-Hill, New York (1941).

[4] R. Daudel, R. Lefebre and C. Moser, "Quantum Chemistry Method and Application," Interscience Pub., New York (1963); A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley, New York (1961).

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

played by each atomic orbital during the electronic interaction of this process.

The Parameters Used and the Coordinates

The MO's to describe these systems are represented by a linear combination of valence AO's; that is, the 1s orbital of the hydrogen atom, the 2s, 2px, 2py and 2pz orbitals of the carbon atom, and the 3s, 3px, 3py and 3pz orbitals of the chlorine atom.

The Coulomb integrals of these AO's, H_{ii}, are given as follows:

$$H_{ii}(\mathrm{1s, H}) = -13.60\ \mathrm{eV.}$$
$$H_{ii}(\mathrm{2s, C}) = -21.43\ \mathrm{eV.}$$
$$H_{ii}(\mathrm{2p, C}) = -11.42\ \mathrm{eV.}$$
$$H_{ii}(\mathrm{3s, Cl}) = -25.26\ \mathrm{eV.}$$
$$H_{ii}(\mathrm{3p, Cl}) = -15.09\ \mathrm{eV.}$$

These values are cited from Pritchard and Skinner's paper⁽⁶⁾ while that of the 3s orbital of the chlorine atom is estimated by means of the observed atomic spectra.⁽⁷⁾ For the negative chlorine ion, the values of H_{ii} is tentatively assumed to be same as that of the neutral atom.

The resonance intergral between ith and jth AO's, H_{ij}, is calculated by the equation:

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$$

where S_{ij} is the overlap integral and where the value of K is taken to be 1.75 as in Hoffmann's paper.⁽⁵⁾

The effective nuclear charges for these atoms are $Z_{\mathrm{H}} = 1.00$, $Z_{\mathrm{C}} = 3.25$ and $Z_{\mathrm{Cl}} = 6.10$ (for both the ionic and neutral chlorine atoms).

The coordinates of this system are presented in Fig. 1, where the carbon atom is situated at the origin of the coordinate system and where the line of $\mathrm{Cl_2}$-C-$\mathrm{Cl_1}$ is taken as the Y axis. (The symbol $\mathrm{Cl_2}$ refers to the attacking chlorine atom, while $\mathrm{Cl_1}$ refers to the one in the isolated methyl chloride at the initial stage of reaction.) The $\mathrm{Cl_1}$-C-$\mathrm{H_1}$ plane lies in the Y-Z plane, and the angle of $\mathrm{Cl_1}$-C-H is named θ. The C-$\mathrm{H_2}$ bond inclines in the +X direction, and the C-$\mathrm{H_3}$ bond, in the −X direction. The px, py, and pz orbitals of the carbon and chlorine atoms direct their positive parts in the X, Y and Z directions respectively.

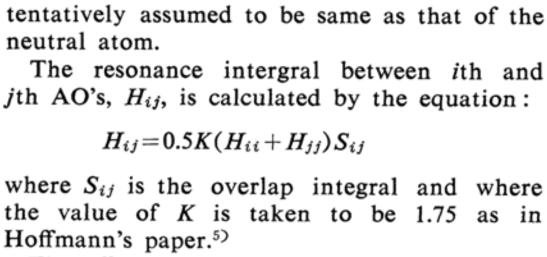

Fig. 1. The coordinate.

The Electronic Structure of the CH$_3$Cl Molecule

The calculated MO energies (in units of eV.), together with their irreducible representation and the values of the coefficients of the AO's of $\mathrm{CH_3Cl}$, are summarized in Table I, where the geometry of this molecule is given as follows:⁽⁸⁾ The C-H distance is 1.1Å, the C-Cl distance is 1.784Å and the angle of Cl-C-H, θ, is 110°, and the molecule belongs to the C_{3v} point group.

Frost and McDowell,⁽⁹⁾ in their electron impact experiment, studied the electronic structure of methyl chloride; they give the electronic configuration of this molecule as $(a_1)^2(a_1)^2(e)^4(a_1)^2(e)^4$, where the MO energies, except for the lowest a_1 MO, are −18.71, −13.02, −12.07 and −11.42 eV. respectively, and where the bracket (A) refers to a molecular orbital belonging to the irreducible representation, A. This order of MO energy agrees with our results, as may be seen in Table I. However, our calculated values are uniformly ca. 3 eV. lower than the above-cited experimental values.

As is shown in Table I, the highest occupied orbital of this molecule is a π-type orbital consisting of the chlorine atom and the methyl group, which is the C-H bonding in the methyl group and which is C-Cl antibonding, and the electrons in this orbital are largely localized on the chlorine atom. Thus, this orbital may be characterized as a lone-pair orbital, as in Ref. 9. The lowest vacant orbital is now a σ-type orbital and is strongly antibonding on the C-Cl bond. This result agrees with our previous result.⁽¹⁰⁾ This orbital energy, that is, +1.08 eV., seems to be too high, however, and the energy difference between the highest occupied and the lowest vacant orbitals becomes about 15 eV., while the experimental value, obtained by means of the spectroscopic data, is about 8 eV.⁽¹¹⁾

---

6) H. A. Skinner and H. O. Pritchard, *Chem. Revs.*, 55, 745 (1955).

7) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards, Washington (1949).

8) "Table of Interatomic Distances and Configuration in Molecules and Ions," Ed. by A. D. Mitchell, L. C. Cross, L. E. Sutton and D. G. Jenkin, The Chemical Society, London (1958).

9) D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.*, **A241**, 194 (1957).

10) T. Yonezawa, H. Kato, H. Saito and K. Fukui, This Bulletin, 35, 1814 (1962).

11) M. J. Kamlet, "Organic Spectra Data," Vol. I, Interscience, N. Y. (1960).

TABLE I. MOLECULAR ORBITALS OF CH_3Cl

Irreducible representation	a_1	a_1	e	e	a_1	e^{*1}	e^{*1}	a_1^{*2}
Orbital energy, eV.	−27.78	−21.75	−16.00	−16.00	−15.76	−13.80	−13.80	+1.09
S_C*3	0.427	−0.415	0.0	0.0	0.005	0.0	0.0	0.218
X_C	0.0	0.0	−0.246	0.316	−0.0	−0.293	−0.351	0.0
Y_C	0.064	0.185	0.0	0.0	0.383	0.0	0.0	1.094
Z_C	0.0	0.0	0.316	0.246	0.0	−0.351	0.293	0.0
H_1	0.076	−0.177	0.239	0.186	−0.125	−0.294	0.245	0.171
H_2	0.076	−0.177	−0.281	0.114	−0.125	−0.066	−0.378	0.171
H_3	0.076	−0.177	0.041	−0.300	−0.125	0.359	0.132	0.171
S_{Cl}	0.676	0.644	0.0	0.0	−0.117	0.0	0.0	−0.585
X_{Cl}	0.0	0.0	−0.421	0.542	0.0	0.472	0.565	0.0
Y_{Cl}	−0.030	0.213	0.0	0.0	−0.784	0.0	0.0	0.764
Z_{Cl}	0.0	0.0	0.542	0.421	0.0	0.565	−0.472	0.0

*1 The highest occupied orbitals (degenerated).

*2 The lowest vacant orbital.

*3 The symbols S_C, X_C, Y_C and Z_C denote 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} refer to the 3s, 3px, 3py and 3pz orbital of the chlorine atom.

The calculated results for the charge distributions[12] are as follows: The atomic orbital populations, $N(r)$, are:

$$N(S_H)=0.875$$

$$N(S_C)=1.140 \quad N(X_C)=N(Z_C)=1.111 \quad N(Y_C)=0.683$$

$$N(S_{Cl})=1.819 \quad N(X_{Cl})=N(Z_{Cl})=1.998 \quad N(Y_{Cl})=1.513$$

where the notations, S_H, S_C and X_C etc., denote the hydrogen 1s orbital, the carbon 2s and 2px orbitals, and so on. The atomic populations, $M(A)$, are calculated as 4.045 on the carbon atom and as 7.329 on the chlorine atom.

The atomic bond populations, $M(A\text{–}B)$, are $M(C\text{–}H)=0.802$, $M(C\text{–}Cl)=0.564$, $M(H\cdots H)=-0.074$ and $M(H\cdots Cl)=-0.067$. The calculated values of the atomic orbital bond population, $N(r\text{–}s)$, between the r and s atomic orbitals are listed in Table II. For the C–Cl bond, the value of $N(Y_C\text{–}Y_{Cl})$ is 0.338 and is the largest, and the magnitude of $N(Y_C\text{–}S_{Cl})$ and $N(S_C\text{–}Y_{Cl})$ is of the same order, while $N(X_C\text{–}X_{Cl})$ and $N(Z_C\text{–}Z_{Cl})$ are both negative and very small.

TABLE II. THE $N(r\text{–}s)$ VALUES BETWEEN AO's OF THE C–Cl AND C–H BONDS IN CH_3Cl

	S_C	X_C	Y_C	Z_C
S_{Cl}	0.022	0	0.142	0
X_{Cl}	0	−0.034	0	0
Y_{Cl}	0.128	0	0.338	0
Z_{Cl}	0	0	0	−0.034
H_1	0.238	0	0.048	0.517
H_2	0.238	0.388	0.048	0.129
H_3	0.238	0.388	0.048	0.129

Accordingly, the C–Cl bond is a σ-type bond and is mainly dependent upon the interaction between the carbon 2py orbital and the chlorine 3py orbital, whereas the 3px and 3pz orbitals of the chlorine atom do not participate in the bond formation and stand for lone-pair orbitals. On the other hand, the $N(r\text{–}s)$ values of the pairs between AO's of C–H bond indicate that the carbon 2px and 2pz orbitals do participate in the C–H bonding and not in the C–Cl bonding.

The Electronic Structure of the "Transient Species" $(Cl\cdots CH_3\cdots Cl)^-$

In this section, we will treat, on the assumption of adiabaticity, the electronic structure of the systems in which the attacking chlorine ion (Cl_2) interacts with the isolated methyl chloride with various assumed configurations. It is well established, in normal S_N2-type halogen substititions of alkyl halides, that the replacement proceeds most often in such a way that the attacking reagent, the central carbon atom and the substitution atom lie co-linear and the hybridization of the central carbon atom shifts from sp^3 to sp^2, which is finally reached in the transition state. However, the reaction path of this reaction has not yet been strictly established. Accordingly, we have tentatively selected two hypothetical processes, a and b, and have investigated the electronic structure of the species $(Cl\cdots CH_3\cdots Cl)^-$. This is neither a stable molecule nor an unstable intermediate,

---

[12] K. Morokuma, H. Kato, T. Yonezawa and K. Fukui, This Bulletin, 33, 1263 (1965).

but rather corresponds to a certain configuration near the transition state. The electronic structure is calculated with respect to several different configurations in each process. These calculated configurations are shown in Table III, together with the calculated total electronic energy values (in eV.), where the C–Cl$_1$ bond distance is denoted as r_1 and the C–Cl$_2$ distance as r_2, and where the Cl$_1$–C–H angle is θ. The C–H distances are kept constant, as equal to 1.10Å throughout both the a and b processes. In both processes a chlorine ion approaches the isolated methyl chloride along the Y axis from the $-$Y direction, as may be seen in Fig. 1, and these two processes start at $r_2=3.0$Å, $r_1=1.784$Å and $\theta=110°$; the process a ends with $r_2=r_1=2.20$Å and $\theta=90°$, and the process b with $r_2=r_1=2.05$Å and $\theta=90°$ (Ingold et al.[2]) adopted the value $r_2=r_1=2.05$Å, and Spinner,[13]) 2.17Å, as the C–Cl bond distances at the transition state of the chlorine substitution reaction of methyl chloride.).

TABLE III. THE VARIOUS CONFIGURATIONS AND THE CALCULATED TOTAL ELECTRONIC ENERGY VALUES (eV.) IN THE $(\mathrm{Cl}\cdots\mathrm{CH_3}\cdots\mathrm{Cl})^-$ SYSTEMS

r_1 Å	r_2 Å	θ °	Total energy eV.
1.784	3.0	90	−389.07
		100	−390.15
		110	−390.36
1.9	2.8	95	−390.15
		100	−390.43
		110	−390.34
2.0	2.6	95	−390.08
		100	−390.20
		110	−389.80
2.1	2.4	90	−389.46
		95	−389.60
		100	−389.52
2.15	2.3	90	−389.18
		95	−389.20
		100	−388.99
2.2	2.2	90	−388.85
		95	−388.73
		100	−386.96
1.85	2.8	100	−390.17
		110	−390.36
1.9	2.6	95	−389.52
		100	−389.73
		110	−389.48
1.95	2.4	95	−388.71
		100	−388.77
		110	−388.14
2.0	2.2	90	−387.16
		95	−387.25
		100	−387.05
2.05	2.05	90	−386.01
		95	−385.85

When we refer to the calculated values of the total electronic energies in Table III, we can see that those values have a minimum, with a variation of θ at fixed r_1 and r_2 distances. This may tentatively be referred to as a "local" minimum. The value of θ at local minima gradually decrease from 110° at the initial state to 90° at the symmetrical configuration ($r_1=r_2$, $\theta=90°$).

For the sake of simplicity, several sets of r_1 and r_2 values were selected for each process, a and b. The electronic structure was calculated with respect to the configurations in which the value of θ corresponds to a local minimum at this fixed r_1 and r_2. These configurations are summarized in Table IV, where they are named a-I, a-II,⋯, a-VI and b-I, b-II, ⋯, b-VI respectively (a-I and b-I have the same configuration.).

Now let us investigate the process of the nucleophilic reaction of aliphatic compounds. The configurations which we adopted allow

TABLE IV. THE SELECTED CONFIGURATION AND THE CALCULATED VALUES OF THE TOTAL ELECTRONIC ENERGY (eV.) E, AND THE ATOMIC POPULATION, M(A), OF EACH ATOM IN THE a and b PROCESSES

Process	r_1	r_2	θ	E	M(C)	M(H)	M(Cl$_1$)	M(Cl$_2$)
a-I	1.784	3.0	110	−390.36	4.056	0.872	7.333	7.995
II	1.9	2.8	100	−390.43	3.986	0.869	7.413	7.994
III	2.0	2.6	100	−390.20	3.924	0.869	7.491	7.979
IV	2.1	2.4	95	−389.60	3.852	0.868	7.618	7.925
V	2.15	2.3	95	−389.20	3.829	0.869	7.691	7.873
VI	2.2	2.2	90	−388.85	3.820	0.870	7.784	7.784
b-I	1.784	3.0	110	−390.36	4.056	0.872	7.333	7.995
II	1.85	2.8	100	−390.17	4.013	0.869	7.386	7.995
III	1.9	2.6	100	−389.73	3.979	0.869	7.428	7.986
IV	1.95	2.4	100	−388.77	3.938	0.869	7.492	7.961
V	2.0	2.2	95	−387.25	3.882	0.874	7.611	7.883
VI	2.05	2.05	90	−386.01	3.862	0.880	7.749	7.749

---

13) E. Spinner, *Aust. J. Chem.*, **13**, 218 (1960).

TABLE V. THE CALCULATED ATOMIC ORBITAL POPULATION, $N(\mathrm{r})$, VALUES ON THE CARBON AND CHLORINE ATOMS IN THE a AND b PROCESSES

Process	$N(S_C)$	$N(Y_C)$	$N(X_C)$ $N(Z_C)$	$N(S_{Cl_1})$	$N(Y_{Cl_1})$	$N(X_{Cl_1})$ $N(Z_{Cl_1})$	$N(S_{Cl_2})$	$N(Y_{Cl_2})$	$N(X_{Cl_2})$ $N(Z_{Cl_2})$
a-I	1.149	0.680	1.113	1.820	1.516	1.998	1.998	1.999	1.999
II	1.184	0.627	1.087	1.869	1.543	2.000	1.999	1.996	1.999
III	1.206	0.538	1.090	1.904	1.587	2.000	1.998	1.984	1.998
IV	1.227	0.453	1.086	1.938	1.680	2.000	1.990	1.937	1.998
V	1.234	0.421	1.087	1.952	1.740	2.000	1.983	1.894	1.998
VI	1.236	0.414	1.085	1.968	1.818	2.000	1.968	1.818	2.000
b-I	1.149	0.680	1.113	1.820	1.516	1.998	1.998	1.999	1.999
II	1.175	0.665	1.086	1.851	1.535	2.000	2.000	1.997	1.999
III	1.189	0.612	1.089	1.871	1.556	2.000	1.999	1.991	1.998
IV	1.205	0.546	1.093	1.894	1.598	2.000	1.996	1.971	1.997
V	1.219	0.485	1.089	1.923	1.689	2.000	1.982	1.906	1.997
VI	1.219	0.466	1.089	1.953	1.799	2.000	1.953	1.799	2.000

us to derive a certain semi-quantitative conclusion concerning the electronic distribution in the process of the reaction.*

The Electronic Energy and the Atomic Population.—The calculated values of the total electronic energy (in eV.) and the atomic population, M(A), of each atom in these configurations in both processes are given in Table IV. The calculated results show that, in both processes, the total energies become higher and higher as the C–Cl_2 distance decreases.

On the other hand, the calculated values of M(A) lead to the following results: The $M(Cl_2)$ values decrease from 7.995 at the initial state to 7.784 at the a-VI state, while the M(C) values decrease from 4.056 to 3.820 and the $M(Cl_1)$ values increase from 7.333 to 7.784 through the process a. This tendency is similar to that in the process b. That is, the negative charge located on the chlorine ion at the initial configuration gradually migrates to the Cl_1 atom, and at the symmetrical configuration the M(A) values of Cl_2 and Cl_1 atoms become equal.

In order to discuss this further, the calculated values of the atomic orbital populations, N(r), of various AO's are collected in Table V, while the relation between the magnitude of N(r) and the configuration at various stages is plotted in Fig. 2. In the process a, $N(S_C)$ increases gradually from 1.149 to 1.236 and $N(Y_C)$ remarkably decreases from 0.680 to 0.414, while the values of the X_C and Z_C orbitals are almost invariable. As for the Cl_1 atom, the change of $N(Y_{Cl_1})$ is the largest, i. e. from 1.516 to 1.818; that of $N(S_{Cl_1})$ is the next, and the N(r) values of X_{Cl_1} and Z_{Cl_1} orbitals are almost constant, i. e., ca. 2.000 through the process a. The N(r) values of the Cl_1 atom show a tendency to be the inverse of that of the Cl_2 atom. Thus, it is noticed that the changes in the M(A) values are mainly governed by that of the 2py orbital at the carbon atom and the 3py orbitals at the chlorine atoms, whereas the N(r) values of the 3px and 3pz orbitals of the chlorine atoms remain constant and these orbitals have a lone-pair orbital, as in nature. These results will be accepted more easily in the light of the discussion in the following section.

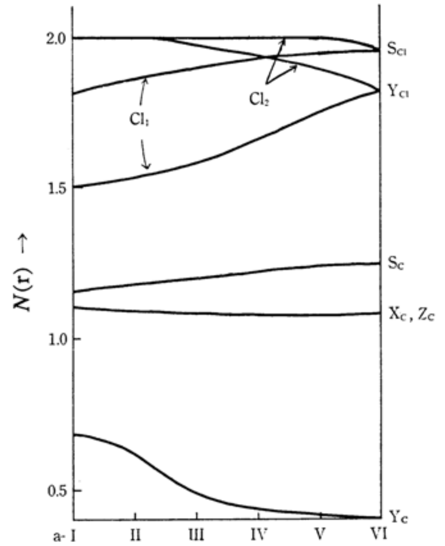

Fig. 2. The change of the N(r) values of the carbon and chlorine atoms through the process a.

The Bond Population in the C–Cl Bond.—Tables VI and VII list, respectively, the calculated values of the atomic bond populations, M(A–B), between various atoms, and also those of the atomic orbital bond populations,

---

* If we adopt the M(A) or M(A–B) values with a little different θ values from those in Tables IV and VI, our conclusions will be not seriously affected, since the variations in these magnitudes are limited within 0.02.

N(r–s), between various AO's. The values of M(C–Cl$_1$) and M(C–Cl$_2$) vary inversely proportionally to their bond distance; both are positive and equal at the symmetrical configuration. The value of M(H–C) shows only a slight change during the course of both processes, a and b, in its overall magnitude, but it varies remarkably in its terms. This point will be discussed again in a later section.

The M(C–Cl$_1$) values decrease rapidly in both processes, that is, from 0.558 to 0.102 in the process a and from 0.558 to 0.098 in the process b. The magnitudes of the contributions of several factors to the rapid decrease in M(C–Cl$_1$) may be roughly estimated as follows: a) The contribution from the change in the θ value. This magnitude may be estimated by the difference between the values of M(C–Cl$_1$) at $r_1=r_2=r_0$, $\theta=90°$, and the value at $r_1=r_2=r_0$, $\theta=110°$. The value of r_0 is taken as 2.20Å in the process a and as 2.05Å in the process b. That is, it is calculated as -0.038 at the process a and at -0.018 at the process b. b) The contribution from the interaction with the Cl$_2$ atom. This magnitude may be estimated by means of the difference between M(C–Cl$_1$) at $r_1=r_2=r_0$, $\theta=90°$, and the value at $r_1=r_0$, $r_2=\infty$ and $\theta=90°$, it is -0.158 in the process a and -0.242 in the process b. c) The contribution from the streching of the C–Cl$_1$ bond. This is estimated by means of the difference between M(C–Cl$_1$) at $r_1=r_0$, $r_2=\infty$, $\theta=110°$, and that at $r_1=1.784°$Å, $r_2=\infty$, $\theta=110°$. This is -0.246 in the process a and -0.160 in the process b. On the basis of these estimations, it may be concluded that the decrease in the M(C–Cl$_1$) value is mainly brought about by the interaction with the Cl$_2$ atom and the streching of the C–Cl$_1$ bond, while the effect of the change in θ is very small.

On investigating the values of N(r–s) in the C–Cl bond given in Table VI and Fig. 3, it may be seen that a remarkable change during the processes is observed in the values of $N(\mathrm{Y_C{-}Y_{Cl_1}})$ and $N(\mathrm{Y_C{-}Y_{Cl_2}})$; i. e., the former decreases and the latter increases in both processes, while there is a less remarkable change in the $N(\mathrm{Y_C{-}S_{Cl_1}})$ and $N(\mathrm{S_C{-}Y_{Cl_1}})$ values. In the symmetrical configuration, the magnitude N(r–s) decreases in the order of $N(\mathrm{Y_C{-}Y_{Cl}})>N(\mathrm{Y_C{-}S_{Cl}})>N(\mathrm{S_C{-}Y_{Cl}})$, where the $N(\mathrm{S_C{-}Y_{Cl}})$ value is negative. Accordingly, the C–Cl bond is considered to be formed mainly through the interaction between the 3py orbitals of the two chlorine atoms and the 2py orbital of the carbon atom. The interaction between the chlorine 3py and the carbon 2s orbitals is not concerned with this bond formation, especially near the symmetrical configuration. The values of $N(\mathrm{X_C{-}X_{Cl}})$ and $N(\mathrm{Z_C{-}Z_{Cl}})$ are almost unchangeable and are negligibly small throughout the process.

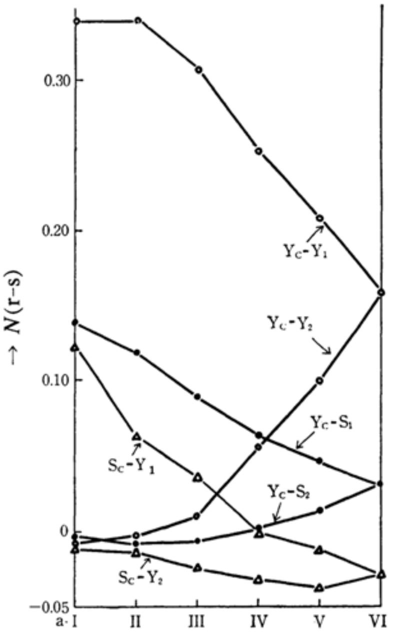

Fig. 3. The change of the N(r–s) values between some AO's of the carbon and chlorine atoms in the process a, where S$_1$ and S$_2$, etc. refer to the 3s orbitals of the chlorine 1 and 2 atom and so on.

The Change of N(r–s) in the C–H Bond.— The N(r–s) values between AO's of the hydrogen and carbon atoms in both processes are

TABLE VI. THE CALCULATED VALUES OF THE ATOM BOND POPULATIONS, M(A–B) IN THE a AND b PROCESSES

Process	C-H	C-Cl$_1$	C-Cl$_2$	H-Cl$_1$	H-Cl$_2$*	Process	C-H	C-Cl$_1$	C-Cl$_2$	H-Cl$_1$	H-Cl$_2$*
a-I	0.804	0.558	−0.026	−0.068	−0.006	b-I	0.804	0.558	−0.026	−0.068	−0.006
II	0.816	0.456	−0.030	−0.064	−0.012	II	0.814	0.486	−0.032	−0.072	−0.012
III	0.822	0.376	−0.040	−0.056	−0.024	III	0.820	0.444	−0.052	−0.066	−0.024
IV	0.830	0.256	−0.010	−0.056	−0.040	IV	0.832	0.380	−0.072	−0.068	−0.048
V	0.834	0.192	0.022	−0.056	−0.052	V	0.844	0.254	−0.028	−0.082	−0.080
VI	0.836	0.102	0.102	−0.060	−0.060	VI	0.854	0.098	0.098	−0.100	−0.100

* The notation, A–B denotes the M(A–B) value between the A and B atoms.

TABLE VII. THE CALCULATED N(r-s), VALUES BETWEEN THE C-Cl_1 AND C-Cl_2 BONDS IN THE a AND b PROCESSES

Process	S-S_1	S-Y_1	X-X_1 Z-Z_1	Y-S_1	Y-Y_1	S-S_2	S-Y_2	X-X_2 Z-Z_2	Y-S_2	Y-Y_2*
a-I	0.020	0.124	−0.034	0.140	0.340	−0.006	−0.008	−0.001	−0.004	−0.006
II	−0.012	0.064	−0.030	0.122	0.340	−0.008	−0.012	−0.002	−0.006	−0.001
III	−0.018	0.038	−0.020	0.092	0.308	−0.016	−0.022	−0.004	−0.004	0.012
IV	−0.030	0.0	−0.018	0.066	0.254	−0.026	−0.030	−0.008	0.004	0.058
V	−0.030	−0.010	−0.014	0.050	0.210	−0.034	−0.036	−0.012	0.016	0.100
VI	−0.036	−0.028	−0.014	0.034	0.160	−0.036	−0.028	−0.014	0.034	0.160
b-I	0.020	0.124	−0.034	0.140	0.340	−0.006	−0.008	−0.001	−0.004	−0.006
II	−0.008	0.076	−0.036	0.138	0.352	−0.008	−0.011	−0.002	−0.006	−0.004
III	−0.015	0.058	−0.030	0.122	0.338	−0.016	−0.020	−0.004	−0.009	0.001
IV	−0.023	0.035	−0.025	0.104	0.314	−0.030	−0.036	−0.009	−0.009	0.021
V	−0.041	−0.004	−0.025	0.083	0.267	−0.047	−0.045	−0.017	0.009	0.088
VI	−0.054	−0.035	−0.025	0.049	0.187	−0.054	−0.035	−0.025	0.049	0.187

* The notations, S, S_1 and S_2··· refer to the 2s orbital of the carbon atom and the 3s orbitals of the chlorine 1 and chlorine 2 atoms and so on.

TABLE VIII. THE CALCULATED N(r-s) VALUES BETWEEN THE H_1-C BOND IN THE a AND b PROCESSES

Process	H_1-S_C	H_1-Y_C	H_1-Z_C*	Process	H_1-S_C	H_1-Y_C	H_1-Z_C*
a-I	0.253	0.026	0.530	b-I	0.253	0.026	0.530
II	0.267	0.021	0.527	II	0.263	0.023	0.528
III	0.280	0.016	0.525	III	0.273	0.021	0.527
IV	0.297	0.005	0.527	IV	0.288	0.017	0.526
V	0.304	0.003	0.527	V	0.310	0.005	0.529
VI	0.309	0.0	0.528	VI	0.322	0.0	0.532

* The notation H_1-S_C denotes the N(r-s) value between the 1s orbital of the hydrogen 1 and the 2s orbital of the carbon atom.

listed in Table VIII, where the H_1 1s orbital does not overlap with the carbon 2px orbital, as is shown in Fig. 1, hence, the $N(H_1-X_C)$ values are omitted in Table VIII. By referring to the calculated results, it may clearly be seen that $N(H_1-S_C)$ values increase and $N(H_1-Z_C)$'s are almost invariable in both processes. Thus, the carbon 2s orbital is concluded to play an important role in the C–H bond-formation near the symmetrical configuration. In other words, in this state the s-nature of the C–H bond increases. This result may correspond to the change in the hybridization of the central carbon atom from sp^3 in the direction of sp^2 at the transition state of the S_N2-type reaction.

The discussions above concerned with the roles of various AO's in the interactions of these systems may be summarized as follows: At the carbon atom, the 2s orbital takes part in the C–H and C–Cl bondings at the initial state, whereas at the symmetrical state it participates only in the C–H bonding. The 2px and 2pz orbitals take part in the C–H bonding only, and the 2py orbital alone contributes always to the C–Cl bonding throughout the process. At the chlorine atoms, the 3s orbitals take part partially in the C–Cl bonding, while the 3py orbitals play a dominant part in the C–Cl bonding. The 3px and 3pz orbitals remain as lone-pair orbitals.

The Energy Levels in the Symmetrical Configuration.—The calculated values of MO energy, their irreducible representation, and those of the coefficients of AO's in the symmetrical configuration (a-VI and b-VI) are listed in Tables IX(i) and (ii), where these systems belong to the D_{3h} point group. The characteristic features of these MO's may be pointed out briefly as follows: The a_1' and a_2'' orbitals are $p\sigma$-type orbitals, the e' orbitals are $p\pi$-type orbitals, and the e'' orbitals are lone-pair orbitals of the chlorine atoms.

Judging from the population analysis in Tables VII and VIII, the a_2'' occupied orbitals may be said to make an important contribution to the C–Cl bonding, while the other MO's make a minor contribution. On the other hand, the highest-occupied orbital belonging to a_1' has a C–Cl antibonding and a C–H bonding character and its energy is very sensitive to the C–Cl distance, which is, in our approximation, interpreted in terms of the magnitude of the overlap between the carbon

TABLE IX. THE MOLECULAR ORBITALS OF THE SYMMETRICAL CONFIGURATION

(i) a-VI State ($r_1=r_2=2.2$ Å, $\theta=90°$)

Irreducible representation	a_1'	a_2''	a_1'	e'	e'	a_2''	e''	e''	e'	e'	a_1'*1	a_2''*2
Orbital energy	−27.26	−25.43	−21.76	−16.02	−16.02	−15.86	−15.09	−15.09	−14.13	−14.13	−13.63	−6.33
S_C	0.410	0.0	0.471	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.168	0.0
X_C	0.0	0.0	0.0	−0.206	0.338	0.0	0.0	0.0	−0.378	0.229	0.0	0.0
Y_C	0.0	0.114	0.0	0.0	0.0	0.311	0.0	0.0	0.0	0.0	0.0	1.034
Z_C	0.0	0.0	0.0	0.338	0.206	0.0	0.0	0.0	−0.229	−0.378	0.0	0.0
H_1	0.097	0.0	0.154	0.301	0.183	0.0	0.0	0.0	−0.170	−0.281	−0.144	0.0
H_2	0.097	0.0	0.154	−0.309	0.169	0.0	0.0	0.0	−0.159	0.288	−0.144	0.0
H_3	0.097	0.0	0.154	0.008	−0.352	0.0	0.0	0.0	0.329	−0.007	−0.144	0.0
S_{Cl}*3	0.488	0.684	−0.519	0.0	0.0	−0.092	0.0	0.0	0.0	0.0	0.132	−0.247
X_{Cl}*3	0.0	0.0	0.0	−0.237	0.389	0.0	0.0	−0.707	0.466	−0.282	0.0	0.0
Y_{Cl}*3	−0.022	0.007	−0.147	0.0	0.0	−0.611	0.0	0.0	0.0	0.0	−0.711	0.426
Z_{Cl}*3	0.0	0.0	0.0	0.389	0.237	0.0	−0.707	0.0	0.282	0.466	0.0	0.0

(ii) b-VI State ($r_1=r_2=2.05$ Å, $\theta=90°$)

Irreducible representation	a_1'	a_2''	a_1'	e'	e'	a_2''	e''	e''	e'	e'	a_1'*1	a_2''*2
Orbital energy	−27.76	−25.51	−20.95	−16.26	−16.26	−15.99	−15.08	−15.08	−13.76	−13.76	−12.61	−3.52
S_C	0.416	0.0	−0.443	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.208	0.0
X_C	0.0	0.0	0.0	−0.211	0.321	0.0	0.0	0.0	−0.335	0.313	0.0	0.0
Y_C	0.0	0.137	0.0	0.0	0.0	0.310	0.0	0.0	0.0	0.0	0.0	1.083
Z_C	0.0	0.0	0.0	0.321	0.211	0.0	0.0	0.0	−0.313	−0.335	0.0	0.0
H_1	0.089	0.0	−0.145	0.289	0.190	0.0	0.0	0.0	−0.229	−0.245	−0.197	0.0
H_2	0.089	0.0	−0.145	−0.309	0.155	0.0	0.0	0.0	−0.098	0.321	−0.197	0.0
H_3	0.089	0.0	−0.145	0.020	−0.345	0.0	0.0	0.0	0.327	−0.076	−0.197	0.0
S_{Cl}*3	0.473	0.673	0.524	0.0	0.0	−0.112	0.0	0.0	0.0	0.0	0.206	−0.311
X_{Cl}*3	0.0	0.0	0.0	−0.249	0.379	0.0	0.0	−0.707	0.402	−0.375	0.0	0.0
Y_{Cl}*3	−0.023	0.010	0.215	0.0	0.0	−0.601	0.0	0.0	0.0	0.0	−0.701	0.474
Z_{Cl}*3	0.0	0.0	0.0	0.379	0.249	0.0	−0.707	0.0	0.375	0.402	0.0	0.0

*1 The highest occupied orbital.

*2 The lowest vacant orbital.

*3 The notation, S_{Cl} and Y_{Cl} denote ($S_{Cl_1}+S_{Cl_2}$) and ($Y_{Cl_1}+Y_{Cl_2}$) in the a_1' orbitals and ($S_{Cl_1}-S_{Cl_2}$) and ($Y_{Cl_1}-Y_{Cl_2}$) in the a_2'' orbitals, for X_{Cl} and Z_{Cl}, they represent ($X_{Cl_1}+X_{Cl_2}$) and ($Z_{Cl_1}+Z_{Cl_2}$) in the e' orbitals and ($X_{Cl_1}-X_{Cl_2}$) and ($Z_{Cl_1}-Z_{Cl_2}$) in the e'' orbitals respectively.

and chlorine atoms. Thus, this orbital originates from the splitting of the a_1 lowest vacant orbital of the isolated methyl chloride. The mode may be represented by the scheme:

$$a_1(C_{3v}) \rightarrow a_1' \text{ and } a_2'' \ (D_{3h})$$

Accordingly, it may be said that the unstable character and the C–Cl lengthened bond result mainly from this kind of orbital, a_1'.

From the above-mentioned results, it may be concluded that the a_2'' orbitals play an important role in the stabilization of these systems,[4)] but that the a_1' orbitals should be taken into account in the more rigorous treatment.

Summary

The electronic structures of CH_3Cl and a "transient" species $(Cl\cdots CH_3\cdots Cl)^-$ have been calculated by an extended Hückel method. The calculated results of CH_3Cl correlate well with the experimental facts. The main features of the electronic structure of $(Cl\cdots CH_3\cdots Cl)^-$ may be summarized as follows:

1) The 3py orbitals of the chlorine atoms and the 2py orbital of the central carbon atom (pσ-orbitals) play an important role in the interaction between the C–Cl bonds.

2) The 2s orbital of the central carbon atom at the symmetrical configuration makes no contribution to the C–Cl bonding; rather, this orbital, together with the 2px and 2pz orbitals, participates in the C–H bonding.

3) The 3px and 3pz orbitals of the chlorine atoms form the lone-pair orbitals.

The natures of the MO's of the symmetrical configuration have also been briefly discussed.

It should be noticed, however, that the present treatment is not yet sufficiently qualified as a method to allow an interpretation of the stable configuration of a molecular system, since it does not explicitly take into account the nuclear repulsion and the electronic interaction. Accordingly, there remains room for criticism with respect to the theoretical significance which the configuration of such a local minimum will have in the true electronic process on the reaction path. This point will be examined further in the future.

The calculations have been carried out on an IBM 7090 computer at the Japan IBM Co., with the permission of the UNICON committee, which the authors wish to thank.

Department of Fuel Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto