A Functional Representation of the Potential Energy Surface of Non-Identical S_N2 Reaction: F⁻ ··· CH₃Cl → FCH₃ ··· Cl⁻

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The potential energy surface (PES) of the non-identical S_N2 reactions, F⁻+CH₃Cl→FCH₃+Cl⁻ and (H₂O)F⁻ + CH₃Cl→FCH₃+Cl⁻ (H₂O), were investigated with ab initio MO calculations. The *ab initio* minimum energy reaction path (MERP) of the F⁻+CH₃Cl→FCH₃+Cl⁻ was obtained and it was expressed with an intermediate variable t. The *ab initio* PES was obtained near around t. Analytical potential energy function (PEF) was determined as a function of the t in order to reproduce the *ab initio* PES. Based on Morse-type potential energy function, a Varying Repulsive Cores Model (VRCM) was proposed for the description of the bond forming and the bond breaking which occur simultaneously during the S_N2 reaction. The MERP calculated with the PEF is well agreed with the *ab initio* MERP and PEF could reproduce the *ab initio* PES well. The potential parameters for the interactions between the gas phase molecules in the reactions and water were also obtained. ST2 type model was used for the water.

Introduction

The studies on the PES of the chemical reaction between ions and molecules have widely investigated and have yielded many useful informations for the understanding of various fields in chemistry. Especially, bi-molecular nucleophilic substitution (S_N2) reactions[1] are most widely studied in chemistry and the basic properties of the mechanism have been well known for a long time.

Although many informations about the PESs of the S_N2 reactions were obtained from theoretical studies[2-17] and experimental investigations,[18-23] the functional representation of the PESs[11-13,24] is remained as a major task to be done, for it is very useful for the dynamic and statistical studies on the S_N2 reactions in both gas phase and aqueous solution.

For identical S_N2 reactions, especially Cl⁻+CH₃Cl→ClCH₃ +Cl⁻, Chandrasekhar, Smith and Jørgensen,[13] Van de Linde and Hase,[11] and Tucker and Tuchlar[12] developed the analytical potential energy functions.

Chandrasekhar *et al.*[13] obtained a set of analytical PEFs which are defined along MERP, only with one degree of freedom. They introduced an alternative definition of the reaction coordinate, r_C.

$$r_C = r_{Cl-C} - r_{C-Cl} \qquad (1)$$

where r_{Cl-C} and r_{C-Cl} are the distances between Cl⁻ and C, and between C and Cl within C_{3v} symmetry restriction. The energy along MERP was described with this reaction coordinate, r_C.

$$E = E(r_C) \qquad (2)$$

Geometric parameters, net atomic charges, and intermolecular potential parameters were described by the same functional form, as a function of r_C (or r_{C-Cl}).

$$f(r_{C-Cl}) = k_1 \cdot g(r_{C-Cl}) + k_2 \qquad (3)$$

Since r_C was defined only along MERP, $E(r_C)$ and $f(r_{C-Cl})$ are valid only on MERP. They carried out Monte Carlo simulation for a solute cluster solvated by 250 water molecules by using Eqs. (2) and (3) and they derived solute-solvent potential functions from *ab initio* calculations in conjunction with TIP4P water model.

Van de Linde *et al.*[11] expanded the potential energy surfaces with multidimensional analytical potential energy function. They introduced four dependent geometrical parameters, r_{Cl-C}, r_{C-Cl}, $g_a = r_{Cl-C} - r_{C-Cl}$, $g_b = r_{C-Cl} \cdot r_{Cl-C}$, for describing the PEFs and besides some switching functions were introduced for the smooth connection between long-range and short-range potential terms. Since, in this formalism, r_{Cl-C}, r_{C-Cl}, angle H-C-Cl and angle Cl-C-Cl are used as independent geometrical parameters, the potential energy functions can be used for the potential energy surface calculations around MERP different from the potential energy function of Chandrasekhar *et al.*[13] With this PEF, the reaction path calculation and the variational transition state calculations on cluster association, cluster dissociation, and cluster isomerization were performed.

Tucker *et al.*[12] introduced the three-body potential function for the expansion of the PES. Since the Walden inversion, umbrella mode, is strongly coupled with the reaction coordinate, they regarded the angle Cl-C-Cl as one of the main coordinates contributing to the reaction coordinate. The PEF has two main parts as fallows.

$$V_{Tot} = V^{3B} + V_{Vib} \qquad (4)$$

where V^{3B} is the three body term where the methyl group was treated as a single particle and V_{Vib} is the additional potential part due to the hydrogen vibrations. V^{3B} was given by

$$V^{3B} = V^{LEPS} + V^{LR} + V^0 \qquad (5)$$

where V^{LEPS}, V^{LR} and V^0 are three-body extended LEPS[25]

potential, long-range electrostatic interaction, and reference potential, respectively. For V^{LEPS}, three geometrical parameters, $r_{Cl^-\text{-}Cl}$, $r_{Cl^-\text{-}C}$ and $r_{C\text{-}Cl}$, were used, and for calculating V^{LR}, the net atomic charges were expressed with r_C, and the force constants in V^0 were also described as functions of r_C. Especially, the polarization energy was included in the total energy, V_{Tot}, and the polarizabilities were expressed as linear functions of net atomic charges. With this PEF, the semi-empirical potential energy surface for the reaction was calculated and the rate constant and the activation energy of the reaction were estimated at several temperatures.

The purpose of this work is the functional representations of the *ab initio* PES of the following non-identical S_N2 reactions through least-squares fitting procedure. Since the changes in the reaction rate of reaction (6) and the methyl-halide reaction system upon hydration are several orders of magnitude, the PESs for both reactions, (6) and (7), will be investigated.

$$F^- + CH_3Cl \rightarrow FCH_3 + Cl^- \tag{6}$$

$$F^-\cdots Water + CH_3Cl \rightarrow FCH_3 + Cl^-\cdots Water \tag{7}$$
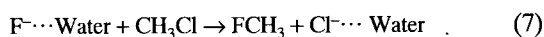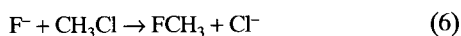
Method

Coordinates for the Reaction Systems.

In this study, a set of internal coordinates (Figure 1 and 2) were used for the description of the reaction systems, Eqs. (6) and (7). The coordinates were classified into two classes according to their degrees of contribution to the MERP of the reaction. The conformations of the complex on the MERP were kept in the C_{3v} symmetry. Whereas the deviations from the C_{3v} symmetry were described with the displacements, $\vec{q}$, from the MERP.

$$\vec{P} = P(\vec{Q}, \vec{q}) \tag{8}$$

where $\vec{Q}$ represents the minimal coordinates which are necessary for describing the C_{3v} conformations. The $\vec{Q}$ is composed of four geometrical parameters, R_{CF}, R_{CCl}, R_{CH} and θ, as shown in Figure 1-a. The equilibrium distance of R_{CH} was assumed to be constant during the reaction for simplicity. Then $\vec{Q}$ is R_{CF}, R_{CCl}, R_{CH} and θ. Once the C_{3v} symmetry is broken as shown in Figure 1-b, one need a reference axis to define the angle θ because the principle axis does no longer. The reference axis is defined as the line perpendicular to the plane formed by the three methyl
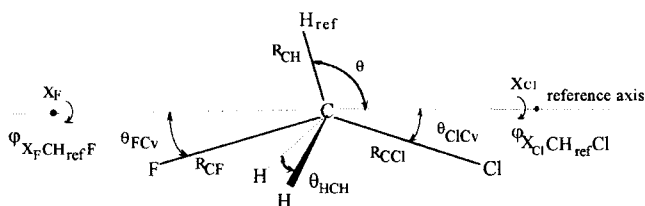
Figure 1. The internal coordinates which were introduced for the gas phase reaction. The reference axis was obtained as the line which is perpendicular to the plane formed by the three hydrogen atoms and passes through the carbon center. The dummy points X_F and X_{Cl} are arbitrary two points located on reference axis and on both sides of the carbon atom.
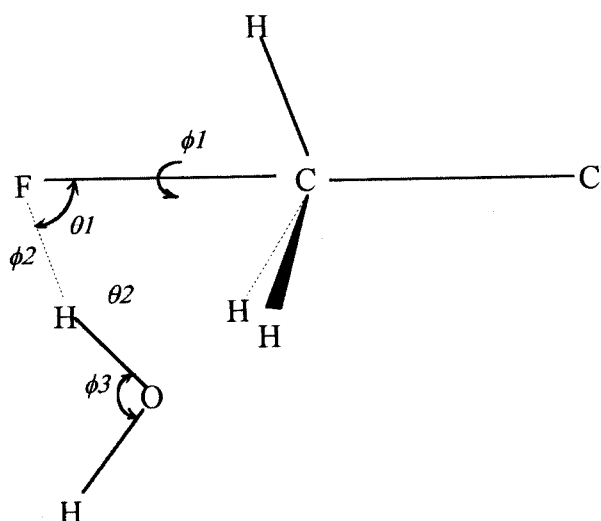
Figure 2. The internal coordinates which were introduced for the description of the S_N2 reaction with one water molecule environment.

hydrogen and passes the center of the carbon atom. The angle θ is defined as the average of the three angles, $\theta_{H_1CX_{Cl}}$, $\theta_{H_2CX_{Cl}}$ and $\theta_{H_1CX_{Cl}}$. X_F and X_{Cl} are the arbitrary points on the reference axis each side of the carbon. θ_{X_FCF} and θ_{X_FCCl} are the angles between the reference axes with C-F and with C-Cl, respectively. Torsional angle $\phi_{X_FH_1CF}$ is the angle between the X_FH_1C plane and C-F bond. $\phi_{X_{Cl}H_1CCl}$ is the angle between the $X_{Cl}H_1C$ plane and C-Cl bond.

Twelve internal coordinates, θ_{H_1CCl}, θ_{H2CCl}, θ_{H_3CCl}, three R_{CH}, θ_{X_FCF}, $\theta_{X_{Cl}CCl}$, $\phi_{X_FH_1CF}$, $\phi_{X_{Cl}H_1CCl}$, R_{CF}, and R_{CCl}, are divided into two parts. The first part is for the C_{3v} conformations, $\vec{Q}(R_{CF}, R_{CCl}, \theta)$ and the second part is for the deviations from C_{3v} conformations, $\vec{q}(\Delta\theta_{H_1CH_3}, \Delta\theta_{H_1CH_2}, \Delta\theta_{X_FCF}, \Delta\theta_{X_{Cl}CCl}$, three ΔR_{CH}S, $\Delta\phi_{X_FH_1CF}$, $\Delta\phi_{X_{Cl}H_1CCl})$. Then a conformation corresponds to a point $\vec{P}$ in a geometric parameter space can be described by the two coordinate sets $\vec{Q}$ and $\vec{q}$ as in Eq. (8).

The point on the MERP, S, can be expressed as follows.

$$S = (R_{CF}^S, R_{CCl}^S, \theta^S) \equiv \vec{Q}^S \tag{9}$$

Since S is a continuous line in three dimensional space $\vec{Q}$, S has a dimension of length. Since the S has only one degree of freedom, $\vec{Q}^S$ can be obtained as a function of the S.

$$\vec{Q}^S = \{R_{CF}(S), R_{CCl}(S), \theta(S)\} \tag{10-a}$$

S can be obtained from the inverse function of (10-a)

$$S = f(R_{CF}, R_{CCl}, \theta) \tag{10-b}$$

and the normal coordinates on the S, $\vec{U}(S)$, become

$$\vec{U}(S) = \sum_{i=1}^{3} (\partial S/\partial Q_i) \, d\vec{Q}_i \tag{11}$$

where Q_i is one of R_{CF}, R_{CCl} and θ. Since one can not exactly describe S with a finite number in the functions of R_{CF}, R_{CCl} and θ, the aproximation of the S coordinate was functionally expressed with R_{CF}, R_{CCl} and θ is designated with symbol t.

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$$S \cong t = f(R_{CF}, R_{CCl}, \theta) \qquad (12\text{-a})$$

$$\vec{Q}^t = \{R_{CF}(t), R_{CCl}(t), \theta(t)\} \qquad (12\text{-b})$$

$$\vec{U}(t) = \sum_{i=1}^{3} (\partial t / \partial Q_i^t) \, dQ_i^t \qquad (13)$$

If the functional forms of the Eq. (12-a) and (12-b) are suitably selected, then the approximate MERP t will be located close to S in the conformational space, $\vec{Q}$.

For the coordinate system of the reaction containing water molecule, Eq. (7), the water molecule was assumed to be rigid and only six internal coordinates [$\vec{W}(r_{FH}, \theta_{CFH}, \theta_{FHO}, \phi_{H_1CFH}, \phi_{CFHO}, \phi_{FHOH})$] were used as in Figure 2.

Ab initio Potential Energy Surface Calculation and Its Functional Representation. The potential energy functions were expressed in terms of the two internal coordinates set $\vec{Q}^t$ and $\vec{q}$. The potential energy at a point ($\vec{Q}^t$, $\vec{q}$) was expressed approximately as the function of t and the deviations from the t. The potential energy was expressed as a sum of the potential energy on the t, $V(t)$, and the contribution due to the deviation from the t.

$$V(\vec{Q}^t, \vec{q}) \cong V(t) + \sum_j k_j(t) \, q_j^2 \qquad (14)$$

$k_j(t)q_j^2$ is the energy contribution due to the deviation from the t.

In this study, all the calculations were restricted to the adiabatic potential energy surface of the lowest singlet states and were performed at the Hartree-Fock level. Several basis sets were tested to examine the theoretical level appropriate for both reactions, Eq. (6) and (7). The heat of reaction of Eq. (1), $(\Delta H_{rxn})^{19\text{-d}}$ and the binding energy of one water to F$^-$ and to Cl$^-$ [$\Delta H_{0\to1}(X^-)$][26] were calculated for each basis set. As shown in Table 1, Anion P functions (AP)[27] on F$^-$ and Cl$^-$ play an important role in eliminating the overestimation of the energies. Among the basis sets tested, four sets, 4-31G with AP, 4-31G* with AP, 6-31G with AP and 6-31* with AP give reasonable energies. Since d-function is important for describing the

Table 1. The heat of reaction and heat of hydration calculated at several basis sets

		D(*)	AP	D+AP
	ΔH_{rxn}^0	-112.6	-138.5	-50.9	-68.0
3-21G	$\Delta H_{0\to1}^0(F^-)$	-52.4	-54.4	-24.1	-25.7
	$\Delta H_{0\to1}^0(Cl^-)$	-16.6	-16.4	-13.8	-13.6
	ΔH_{rxn}^0	-67.1	-63.9	-49.8	-47.1
4-31G	$\Delta H_{0\to1}^0(F^-)$	-36.8	-37.8	-22.9	-23.7
	$\Delta H_{0\to1}^0(Cl^-)$	-18.9	-19.1	-13.2	-13.4
	ΔH_{rxn}^0	-77.3	-74.6	-48.2	-45.1
6-31G	$\Delta H_{0\to1}^0(F^-)$	-34.9	-36.0	-22.6	-23.6
	$\Delta H_{0\to1}^0(Cl^-)$	-14.9	-15.0	-13.4	-10.8

Only F and Cl atoms have polarization orbitals (AP). All the H atoms have 31G basis set and the oxygen atom in water molecules has 3-21G basis set. Experimental values of $\Delta H_{0\to1}^0$ (F$^-$) and $\Delta H_{0\to1}^0$(Cl$^-$) are -23.3 and -13.1 kcal/mole,[23] respectively, and ΔH_{rxn}^0 was obtained as -28 kcal/mole from measurement of the rate constants.[13]

states in the reaction path, 4-31G* with AP basis set was used in this calculations.

Since the conformations of the complex along and around the MERP are statistically more important than the conformations far from the MERP, the *ab initio* calculations were performed for 195 conformations along or near the t coordinate, $P(Q^t, \vec{q})$, for the reaction (6). The MERP was calculated with the C_{3v} constraint. The minimum energy conformations were calculated at every step by decreasing the R_{CF} gradually. The decreasing step, ΔR_{CF}, is 0.1 Å. The trajectory of minimum energy conformations in the Q space corresponds to the S coordinate. *Ab initio* calculations for the reaction (7), the reaction in one water environment were performed for the 95 conformations on t coordinate with one water molecule, $P(Q^t, \vec{W})$. The distances between the sampled points and the t coordinate are less than 2 Å. The sampling was made within 4 Å diameter tube along the t coordinate. For the determination of $k_j(t)$, *ab initio* calculations were performed at two points, $P(\vec{Q}^t(t), \pm dq_j)$, along the t coordinate. Using harmonic oscillator approximation, k_j was expressed as a function of t.

Since the purpose of this work is to represent the PES of the reaction around the MERP, it is necessary to define t values outside of the t coordinate because the potential function is described as a function of t even out sides of the MERP. At a point on the t only one conformation Q^t is uniquely defined whereas several points in the Q space can have the same t value.

$$t = f^{-1}(\vec{Q}) \qquad (15)$$

The potential energy parameters of $V(\vec{Q})$ and the functional form of Q_i's, described by Eq. (12-b), were determined from the minimization of the following function, F_M.

$$F_M = \sum_{l=1}^{N} \{(E_l^{ab} - V_l(t))^2 + W_l(\vec{Q}_l^s - \vec{Q}_l^t)^2\} \qquad (16)$$

where E_l^{ap} and $V_l(t)$ are the *ab initio* energy and the energy calculated from potential energy function V at lth point on or near the t coordinate respectively. And $\vec{Q}_l^s$ and $\vec{Q}_l^s$ are the lth point on the MERP and the point described as a function of t (Eq. 12-a), respectively. W_l represents the statistical significancy of lth point.

Results and Discussion

Determination of $\vec{Q}^t$. In Table 2, the geometries of five points, reactant (R), reactant complex (RC), transition state (TS), product complex (PC) and product (P), and the first derivatives with respect to the S at the five points on the MERP and those on the approximate MERP (t coordinate) are listed. The TS was used as the origin of the MERP; S equals zero at TS. The functional expansion of $\vec{Q}^t$ {$R_{CF}(t)$, $R_{CCl}(t)$, $\theta(t)$} was made *via* the least-squares fitting procedures.

$$R_{CF}(t) = 2.1684 - 0.7152t + 0.2021t^2 - 0.0315t^3$$
$$- 0.0617t^4 + 0.0117t^5 \qquad (17)$$

$$R_{CCl}(t) = 2.1198 + 0.6399t + 0.2799t^2 - 0.1734t^3$$
$$+ 0.0370t^4 + 0.0344t^5 \qquad (18)$$

Table 2. The geometries and their 1st derivatives with respective to S and t

	R	RC	TS	PC	P
$dR_{CCl}(S)$	-	-0.24	0.00	1.29	-
$dR_{CCl}(t)$	-	-0.24	0.00	1.36	-
$dR_{CCl}(S)/\partial S$	0.00	0.20	0.67	1.00	1.00
$dR_{CCl}(t)/\partial t$	0.00	0.22	0.64	0.98	1.00
$dR_{CF}(S)$	-	0.39	0.00	-0.77	-
$dR_{CF}(t)$	-	0.44	0.00	-0.77	-
$dR_{CF}(S)/\partial S$	1.00	-0.98	-0.71	-0.01	0.00
$dR_{CF}(t)/\partial t$	1.00	-0.94	-0.72	-0.02	0.00
$d\theta(S)$	-	0.15	0.00	-0.50	-
$d\theta(t)$	-	0.14	0.08	-0.52	-
$d\theta(S)/\partial S$	-	-0.01	-0.22	-0.01	-
$dq(t)/\partial t$	-	-0.06	-0.20	-0.13	-

$R_{CCl}=dR_{CCl}+2.1198$, $R_{CF}=dR_{CF}+2.1684$. θ(in degree)$=97.9543+(57.2592/R_{CH})d\theta$.
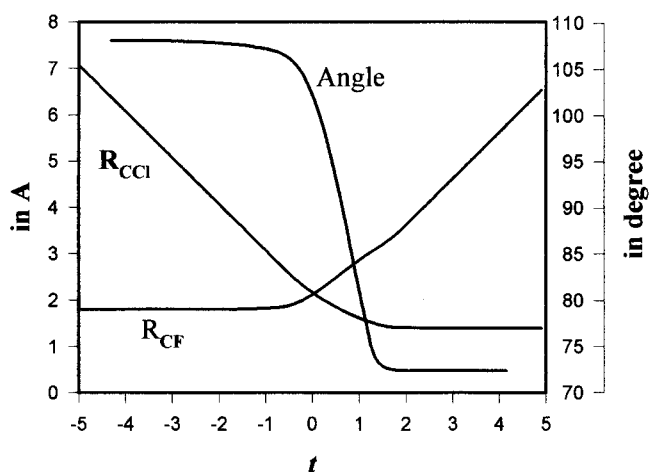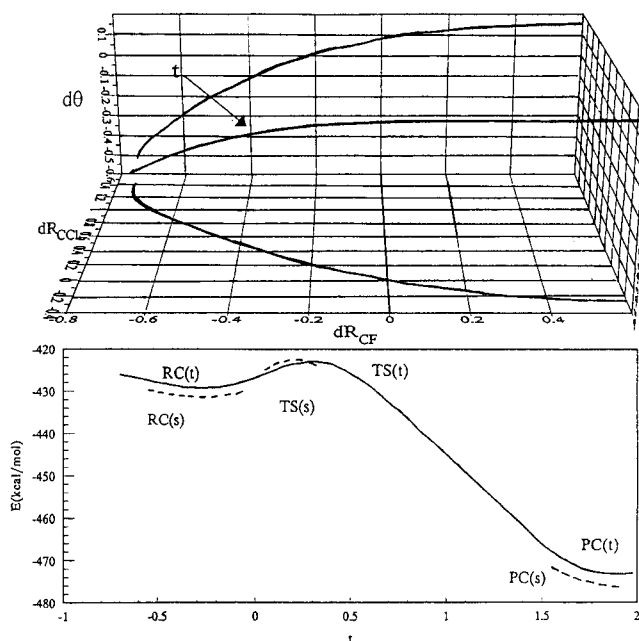
$$\theta(t) = (57.2592/1.07)[-2.0307 \cdot \tanh\{0.1862(t - 0.2793)\}$$
$$-0.0794(t - 0.7293)^2 + 0.0661(t - 0.7293)^3$$
$$+0.0273(t - 0.7293)^4 - 0.1342] + 97.9543 \qquad (19)$$

In Figure 3, the $\vec{Q}^t$ is plotted as the function of the t. In Figure 4, the t is plotted in R_{CF}, R_{CCl} and θ coordinates (upper) and the potential energy, V, is plotted along the t coordinate (lower).

In order to calculate t values near arround the $t(\vec{Q})$ coordinate which corresponds to the Eq. (12-a) was obtained,

$$t(\vec{Q}) = -0.6466R_{CF} -0.0782R_{CF}^2 +0.0056R_{CF}^3$$
$$-0.0995R_{CCl} + 0.2359R_{CCl}^2 - 0.1679R_{CCl}^3$$
$$-0.2395\theta - 0.0023\theta^2 + 9.1529 \qquad (20)$$

Description of the Net Atomic Charges as the Function of the t. For the description of the reaction between ion and the molecule with permanent dipole, accurate estimation of electrostatic interaction is very crucial, because the capturing of the ion by polar molecular occurs

Figure 4. The t is plotted in R_{CF}, R_{CCl}, and θ space (upper) and is projected to θ-R_{CF} and R_{CCl}-R_{CF} planes. The potential energy curves along the t coordinate are plotted (lower).
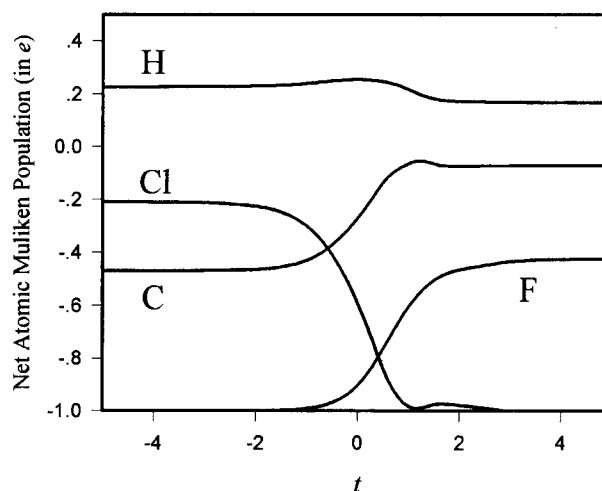
by ion-dipole interaction. In this study, for simplicity, Mulliken population was used as the point charge centered on each atom. Since the Mulliken population changes much during the reaction, the net atomic charges were described as a function of the t.

$$\delta_F(t) = 0.2877 \tanh(1.2475t - 0.7858) -$$
$$[\{2.3962(t - 1.8000)^4\} + 44.0010]^{-1} - 0.7124 \qquad (21)$$

$$\delta_C(t) = 0.1995 \tanh(1.0698t - 0.0432) +$$
$$[\{(-3.6713(t - 0.9000)^4) + 19.0590^{-1}\}] - 0.2702 \qquad (22)$$

$$\delta_H(t) = -0.0290 \tanh(2.4266t - 2.6350) +$$
$$83.2250/(53.410 - 23.7920 \mid t \mid)^2 + 0.1970 \qquad (23)$$

$$\delta_{Cl}(t) = -\{1 + \delta_F(t) + \delta_C(t) + 3\delta_H(t)\} \qquad (24)$$

Figure 3. The changes of the internal coordinates as t. R_{CF} and R_{CCl} are in Å. θ is in degree.

Figure 5. The changes of the net atomic charge and the Mulliken populations are plotted along the t coordinate.

The point charges of each atom are plotted along the t in Figure 5.

Functional Representation of the PES. The PEF in the Q space, $V(Q)$, was described as a sum of several terms.

$$V(\vec{Q}) = V_{el}(\vec{Q}) + V_{orb}(\vec{Q}) + V_{inv}(\vec{Q}) + V_b(\vec{Q}) \qquad (25)$$

where V_{el}, V_{orb}, V_{inv} and V_b represent the electrostatic energy, the electronic energy of the valence electron, the inversion potential of the CH_3 group, and the sum of bonding potential energies of the F$\cdots CH_3$ and the $H_3Cl\cdots C$ pairs, respectively.

The net atomic charges described by Eqs. (21)-(24) were used for the electrostatic energy calculation.

$$V_{el} = \sum_i \sum_{j>i} \delta_i(t) \cdot \delta_j(t) / r_{ij} \qquad (i, j : F, C, H_1, H_2, H_3, Cl) \qquad (26)$$

Since the changes in the valence orbital energy and the net charge of the CH_3 group during the reaction are relatively small compared with those of F and Cl atoms, the contribution of the CH_3 to the V_{orb} was neglected. Therefore the V_{orb} was approximately expressed as

$$V_{orb}(Q) \cong -\delta_F(t)\{E(F^-) - E(F^0)\} - \delta_{Cl}(t)\{E(Cl^-(-E(Cl^0)\} \qquad (27)$$

where $E(X^-)$ and $E(X^0)$ are the electronic energies of negative charged and neutral halogen atom X, respectively. $\{E(F^-)(E(F^0)\}$ and $\{E(Cl^-)-E(Cl^0)\}$ were obtained as -28.828, and -59.553 kcal/mol, respectively.

A harmonic function was used for the inversion potential of the CH_3 group, V_{inv}.

$$V_{inv} = 0.5 k_\theta (\theta - 90)^2 \qquad (28)$$

k_θ was obtained as 0.120 kcal/mol/deg.

Since V_b must contain the driving force for the bond breaking and forming and locating of the TS, the functional form of the V_b is quite complicated. In order to include these factors in the V_b, a Varying Repulsive Core Model (VRCM) was proposed in this study. V_b was expressed as a sum of the bond potentials between CH_3 and X (F or Cl).

$$V_{bond} = \sum_{X=F,Cl} V_{b,X\cdots CH_3}(Q) + E_g \qquad (29)$$

This bond PEF was constructed based on the Morse type function. Since the molecular orbitals and electronic populations of the covalent bonding pairs (F$\cdots CH_3$ and $CH_3\cdots Cl$) change markedly during the reaction, also the potential parameters of the bond PEF must be changed as the reaction proceeds. $V_{v,X\cdots CH_3}$ was expressed as follows.

$$V_{b,X\cdots CH_3}(t, \theta) = D_{e,CX}[e^{-2\alpha_x\{R_{cx}-R_{cx}^0(t,\theta)\}} - 2e^{-\alpha_x\{R_{cx}-R_{cx}^0(\infty,\theta_x)\}}] \qquad (30)$$

where

$$R_{CX}^0(t, \theta) = F_{CX}(t) \, r_{CX}^0(\theta) \qquad (31)$$

where

$$F_{CX}(t) = 1 + c_{CX} e^{-\beta_x \cdot t^2} \qquad (32)$$

and

$$r_{CX}^0(\theta) = r_{CX}^0(\theta_X)(1 + a_{CX} \mid \theta - \theta_X \mid + b_{CX} \mid \theta - \theta_X \mid^2) \qquad (33)$$

In V_b, R^0 s in the Morse type potential are changed as the conformation of the reacting system changes. For the repulsive potential part, the first term in the angle of the Eq. (30), $R_{CX}^0(t, \theta)$ is a function of both t and θ. Since the θ_X is constant, the $R_{CX}^0(t, \theta)$ of attractive part, the second term in the angle of the Eq. (30), becomes constant. $R_{CX}^0(\infty, \theta)$ corresponds to the $R_{CX}^0(\theta_X)$, in Eq. (33). The potential parameters $D_{e,CF}$, $D_{e,CCl}$ and E_g were obtained as 195.27, 131.57 and -158.93 kcal/mole, respectively, and α_{CF} and α_{CCl} were obtained as 1.14546 and 1.46478, respectively. The potential parameters introduced for the description of the varying cores, $r_{CF}^0(\theta_F)$, $R_{CCl}^0(\theta_{Cl})$, a_{CF}, a_{CCl}, b_{CF}, b_{CCl}, c_{CF}, c_{CCl}, β_{CF}, β_{CCl}, θ_{Cl} and θ_{Cl} were obtained as 1.24445 Å, 1.716113 Å, 0.0044917 deg^{-1}, -0.004185 deg^{-1}, 0.00004422 deg^{-2}, -0.000012 deg^{-2}, 0.2602329, 0.09989056, 0.57475031, 0.35666256, 72.0 deg, and 108.0 deg, respectively.

Figure 6 shows the attractive cores at the five points on the t. At the reactant and the product, the repulsive and the interactive cores are coincident. The repulsive core of F$\cdots CH_3$ pair decreases rapidly from the TS to the PC. This rapid decrease of the F$\cdots CH_3$ repulsive core is responsible for the high exothermicity of the reaction and the rapid shortening of the F-C bond. The repulsive core of $CH_3\cdots Cl$ pair does not change much compared with that of F$\cdots CH_3$ through the reaction. The increase of the repulsive core from the TS to the PC is the driving force of the C-Cl bond dissociation.

The MERP of the reaction calculated with the developed potential energy functions is plotted against the R_{CF} in Figure 7. The TS geometry agrees reasonably well with the ab initio results written in parentheses. There are some deviation in the bond length of the R_{CCl} both in the RC and
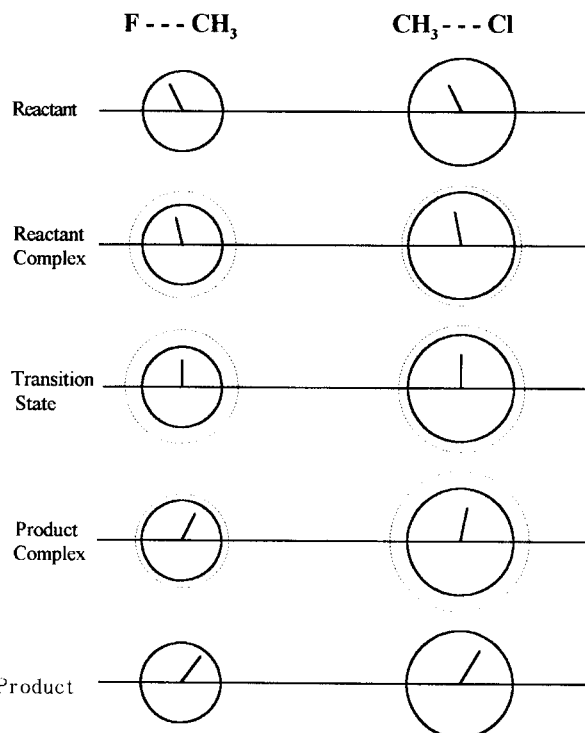
Figure 6. The repulsive cores dotted lines and the attractive cores solid lines of the F and Cl are plotted at the five points, R, RC, TS, PC and P.
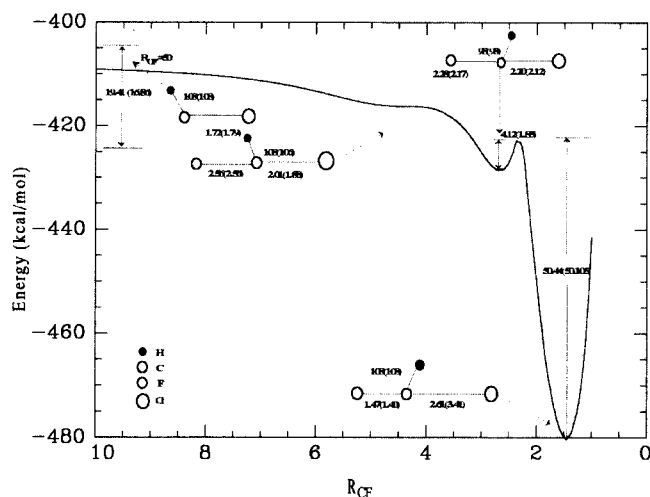
Figure 7. The minimum energy path of the reaction is plotted along the R_{CF}. The values in parenthesis are the energies obtained with ab initio MO calculations.

the PC. The activation energy was obtained as 4.12 kcal/mol with the developed potential energy function. The value of the t on the MERP was calculated with Eq. (20). The energy components of the $V(t)$ are plotted against the t, Figures 8-a and 8-b. The shape of the V_b is similar to that of the total energy, V_{tot}. The V_{orb} and the V_{elec} contribute to the V_{tot} in opposite directions along the t coordinate.

The PEF in the q space, $V(q)$, was described as follows.

$$V(q) = =0.5\sum_j k_j(t)\Delta q_j^2 = 0.5\sum_{i=1}^{3} k_{CH}(t)\Delta R_{CH}^2 + 0.5 k_{HCH}(t)$$

$$(\theta_{H_1CH_2} - 120)^2 + 0.5 k_{HCH}(t)(\theta_{H_2CH_3} - 120)^2$$

$$+ 0.5 k_{X_FCF}(R_{CF})(\theta_{X_FCF})^2 + 0.5 k_{X_aCCl}(R_{CCl})(\theta_{X_aCCl})^2 \qquad (34)$$

where $k_{CH}(t)$ and $k_{HCH}(t)$ are assumed to be constants, 600 kcal/mol·Å^2 and 0.0203 kcal/mol·deg^2, respectively. k_{X_FCF} and k_{X_ClCCl} has the following form.

$$k_{X_iCX}(R_{CX}) = d_X[-tanh\{g_X(R_{CX} - h_X)\} + 1] \qquad (35)$$

where d_F, d_{Cl}, g_F, g_{Cl}, h_F and h_{Cl} were obtained as 0.0384 kcal/mol·deg^2, 0.0304 kcal/mol·deg^2, 2.434 Å^{-1}, 1.520 Å^{-1}, 1.95 Å, and 2.35 Å, respectively. The contribution from the two dihedral angles, $\phi_{X_FH_1CF}$ and $\phi_{X_ClH_1CCl}$, to the potential energy was neglected. It was assumed that the rotation of X with respect to the reference axis does not change the potential energy, except the electrostatic interaction energy.

The PEF of the Reaction with One Water. The interaction between $(F^- \cdots CH_3 \cdots Cl)^-$ and a water molecule, $V(\vec{W})$, is described as follows. In the dispersion-repulsion energy calculation, both the water and the CH$_3$ group were represented by spheres.

$$V(\vec{W}) = \sum_{i=1}^{4}\sum_{j=1}^{6} \delta_i(t)\delta_j(t)/r_{ij} + \sum_l^{F,CH_3,Cl} V_{DR}(r_{l \cdots w}) \qquad (36)$$

where $r_{l \cdots w}$ is the distance between the nonbonding center of the water and F, C or Cl. For electrostatic interactions, charge distribution ST2^{23} type was used for the water molecule (four point charge model) and for the F, C and Cl, atom centered point charges were used. δ_i are described as
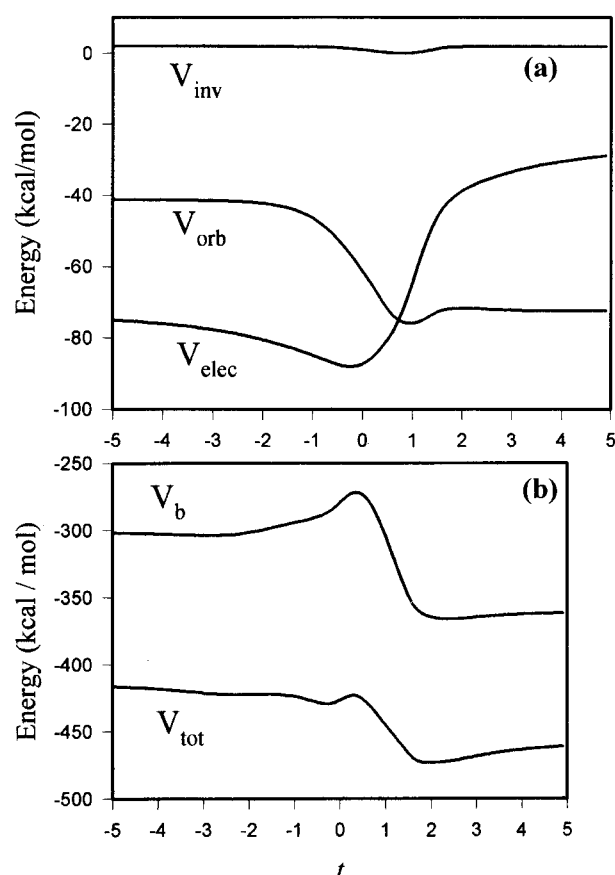
Figure 8. (a) The changes of V_{inv}, V_{orb}, V_{elec}. (b) V_b and V_{tot} are plotted along t coordinate.

the function of the t, Eqs. (21)-(24), whereas the points charges on the water do not change. For the non-bonding interaction, L-J type potential function was used. The l represents one of F, CH$_3$ and Cl. The L-J potential parameters, $\varepsilon_{F \cdots w}$, $\varepsilon_{Cl \cdots w}$ and $\varepsilon_{Cl \cdots w}$ were obtained as 0.674 kcal/mol, 0.921 kcal/mol, and 1.260 kcal/mol, respectively. $\sigma_{F \cdots w}$, $\sigma_{Cl \cdots w}$ and $\sigma_{CH_3 \cdots H}$ were obtained as 2.48 Å, 2.57 Å and 3.02 Å, respectively.

Conclusion

The PES around the MERP was expressed as a function of the approximate MERP coordinate t. The conformations of the reaction system were functionally described with the MERP coordinate. The point charge on each atom was expressed as a function of the t. The changes in the point charges of the F and the Cl during the reaction are 0.5 e and 0.8 e, respectively. The electronic energy of the valance electrons of the F and the Cl are also described as a function of the t. This term is very important for describing the exothermicity of the reaction together with the covalent bond energy, V_b. The VRCM was proposed to describe the simultaneous bond forming and breaking. The MERP of the reaction calculated with the developed potential energy function agreed well with the *ab initio* MERP.

The t value was defined not only on the t coordinate but also near around the t coordinate. The least-square fitting of the PEF was made with the *ab initio* energies of the points

located within 4 Å diameter tube in the Q space. Since the t coordinate locate at the center of the tube, the potential function may work reasonably well not only on the t but also around the t. This potential function can be used for the computer simulation of the reaction without any geometrical constraints.

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