

# Theoretical Studies on Gas-Phase Reactions of F<sup>-</sup> with Fluoroethane: E2 and S<sub>N</sub>2 Reactions

Tsutomu Minato and Shinichi Yamabe\*

Contribution from the Educational Technology Center, Nara University of Education, Takabatake-cho, Nara 630, Japan. Received May 18, 1984

**Abstract:** The gas-phase reactions of F<sup>-</sup> with fluoroethane, E2 and S<sub>N</sub>2 reactions, are investigated by ab initio calculations. The E2 reaction is found to be composed of four elementary processes. They are the first-cluster formation, net E2 reaction producing the second cluster, decomposition of the second cluster, and product formation. In the net E2 reaction, scission of the C-H bond and the C-F bond is synchronous. The S<sub>N</sub>2 reaction is represented by three elementary processes. They are the first-cluster formation, net S<sub>N</sub>2 reaction forming the second cluster, and decomposition of the second cluster. The first cluster of the S<sub>N</sub>2 reaction is different from that of the E2 reaction. Comparison of the E2 reaction with the S<sub>N</sub>2 reaction reveals a preference for the former in the gas phase. The E2 and S<sub>N</sub>2 reactions in solution are discussed on the basis of the calculated results. The theoretical results are compared with experimental data previously reported in the literature, and the possibility of the E1cB mechanism is also discussed.

The present paper describes a theoretical study on bimolecular nucleophilic reactions, elimination (E2), and substitution (S<sub>N</sub>2). Both reactions are fundamental in organic chemistry, and many organic chemists have tackled their study experimentally.<sup>1</sup> Most of these studies deal with reactions in solution. Recently, reactions in the gas phase have been studied by using the ion cyclotron resonance<sup>2</sup> or the flowing afterglow technique.<sup>3</sup> The study of gas-phase reactions gives the intrinsic reactivity of a molecule in the absence of solvent. The intrinsic reactivity corresponds solely to the electronic and structural nature of a molecule. Olmstead and Brauman have suggested a double-well potential for the gas-phase S<sub>N</sub>2 reaction on the basis of their experiments.<sup>4</sup> This double-well potential is well reproduced by ab initio calculations.<sup>5</sup> Thus, ab initio calculations predict the potential energy surface of the gas-phase reaction properly. Atomic motions on the surface give a clue to the understanding of the reaction mechanism. Comparison of the solvent-free data with previously reported results in solution is also useful for studying the solvation phenomena.

In this work, the nucleophilic reaction of fluoride anion (F<sup>-</sup>) with fluoroethane (EtF) is investigated by ab initio calculations. While many theoretical studies on the S<sub>N</sub>2 reaction have been carried out and potential energy surfaces calculated,<sup>5</sup> studies on E2 reactions are rather limited.<sup>6</sup> One reason is that finding the E2 reaction coordinate is difficult because of the many bond alternations in the E2 reaction system. In this paper, we have calculated the potential energy surface of the E2 reaction. Since

the reaction of F<sup>-</sup> with EtF in the gas phase was investigated by Beauchamp et al.,<sup>7</sup> our calculated result is compared with their experiments. Although the E2 reaction usually competes with the S<sub>N</sub>2 reaction in solution, Beauchamp et al. suggested that the E2 reaction occurs exclusively in the gas phase. Comparison of the E2 reaction with the S<sub>N</sub>2 reaction is also made in order to understand the preference of the E2 reaction in the gas phase.

## Computational Method

Computations were carried out with the GAUSSIAN 80 program.<sup>8</sup> Ab initio SCF-MO calculations with the 3-21G+p basis set were made throughout the present work. For carbon and hydrogen atoms, the 3-21G basis set internal to the program was adopted. For a fluorine atom, a set of diffuse p-type GTO's was added to the 3-21G basis set to describe the spread-out electron distribution of F<sup>-</sup>; we used an exponent of 0.074.<sup>9</sup> The double- $\zeta$  + p + p' basis set<sup>10</sup> was also employed to obtain more reliable energetics for the reaction. Stationary points in the reactions were searched for by the gradient method internal to the program. Vibrational analyses on the stationary points obtained were also made to judge whether they gave equilibrium structures or transition states. The analytical first derivatives of the total energy are available in the program. The second derivatives may be obtained by differentiating them numerically. They were calculated by 0.01-au displacement relative to the equilibrium point. When the geometry of the stationary point and all its vibrational frequencies are obtained, the thermochemical quantities  $H^\circ$  and  $S^\circ$  can be calculated by using the standard equations of statistical dynamics.<sup>11</sup>

## Computational Results and Discussion

**Energetics.** The energetics of the E2 reaction of F<sup>-</sup> with EtF is shown in Figure 1. Two reaction schemes are obtained, and both schemes are composed of four elementary processes. At the initial stage of the E2 reaction, F<sup>-</sup> approaches a  $\beta$ -hydrogen of EtF, and the first cluster, F<sup>-</sup>...HCH<sub>2</sub>CH<sub>2</sub>F, is formed. In this text, the word cluster is used to mean a charge-dipole complex. Then, the first cluster isomerizes to the second cluster, HF...C<sub>2</sub>H<sub>4</sub>...F<sup>-</sup>, which can decompose in two ways, separating either into C<sub>2</sub>H<sub>4</sub>

(1) (a) Bartsch, R. A.; Zavada, J. *Chem. Rev.* **1980**, *80*, 453. (b) Baciocchi, E. *Acc. Chem. Res.* **1979**, *12*, 430. (c) Saunders, W. H., Jr. *Ibid.* **1976**, *9*, 19. (d) Bartsch, R. A. *Ibid.* **1975**, *8*, 239. (e) McLennan, D. J. *Tetrahedron* **1975**, *31*, 2999. (f) Fry, A. *Chem. Soc. Rev.* **1972**, *1*, 163. (g) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, N.Y., 1969. (h) Bunton, C. A. "Reaction Mechanism in Organic Chemistry, Vol. 1, Nucleophilic Substitution at a Saturated Carbon Atom", Hughes, E. D., ed.; Elsevier Publishing Co.: London, 1963. (i) Banthorpe, D. V. "Reaction Mechanism in Organic Chemistry, Vol. 2, Elimination Reactions"; Hughes, E. D., Ed.; Elsevier Publishing Co.: London, 1963.

(2) Beauchamp, J. L. *Ann. Rev. Phys. Chem.* **1972**, *22*, 527.

(3) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopt, A. L. *Adv. At. Mol. Phys.* **1969**, *5*, 1.

(4) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(5) (a) Dedieu, A.; Veillard, A. "Quantum Theory of Chemical Reactions"; Daudel, R., Pullman, A., Salem, L., Veillard, A., Eds.; D. Reidel Publishers: New York, N.Y., 1979; Vol. 1. (b) Morokuma, K. *J. Am. Chem. Soc.* **1982**, *104*, 3732. (c) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *Ibid.* **1981**, *103*, 7692, 7694. (d) Bernardi, F.; Schlegel, H. B.; Mislaw, K.; Bottoni, A. *Theor. Chim. Acta* **1977**, *44*, 245. (e) Ishida, K.; Morokuma, K.; Komornicki, A. *J. Chem. Phys.* **1977**, *66*, 2153. (f) Dedieu, A.; Veillard, A. *J. Am. Chem. Soc.* **1972**, *94*, 6730.

(6) (a) Bach, R. D.; Badger, R. C.; Lang, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2845. (b) Lowe, J. P. *Ibid.* **1972**, *94*, 3718. (c) Fujimoto, H.; Yamabe, S.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 971. (d) Fukui, K.; Hao, H.; Fujimoto, H. *Ibid.* **1969**, *42*, 348.

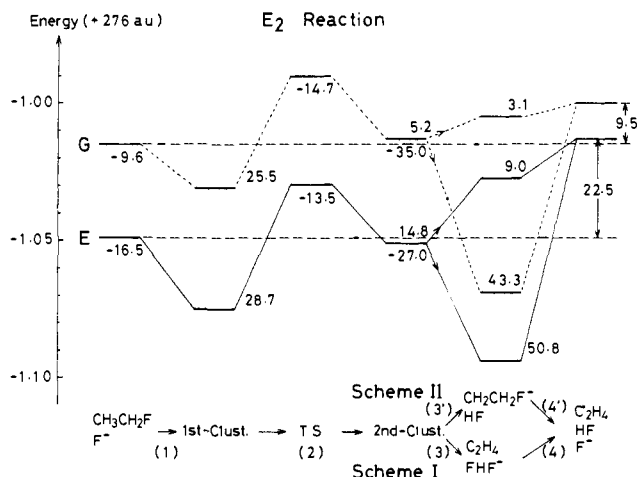
(7) (a) Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 637, 3595. (b) Sullivan, S. A.; Beauchamp, J. L. *Ibid.* **1976**, *98*, 1160.

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

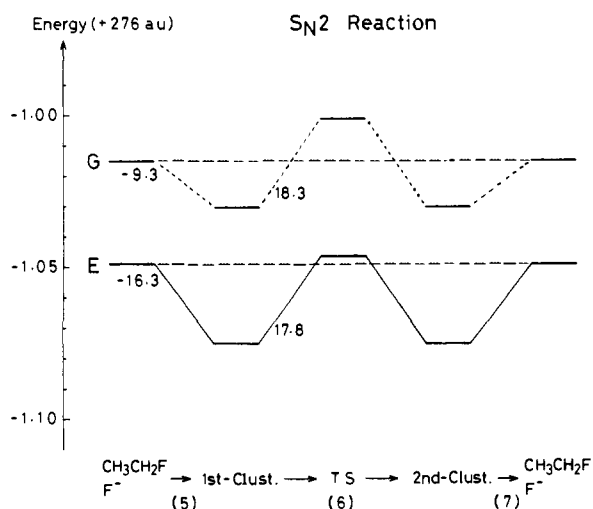
(9) Dunning, T. H., Jr.; Hay, P. J. "Modern Theoretical Chemistry, Vol. 3, Methods in Electronic Structure Theory", Schaefer, H. F., Ed.; Plenum: New York, 1977. Cf.: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294 and the references cited therein.

(10) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823. Also, see ref 9. For a fluorine atom, a set of diffuse p-type GTO's was added to the DZ+p basis set and its exponent was 0.074. This basis set reproduces the hydrogen bond energy for HF and F<sup>-</sup> well. The calculated value is 43.5 kcal/mol, and the observed one is 39 ± 1 kcal/mol. See: Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 5848.

(11) See, for instance: Knox, J. H. "Molecular Thermodynamics"; John Wiley & Sons, Ltd.: New York, NY, 1971.



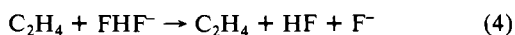
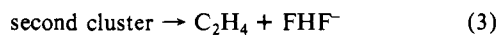
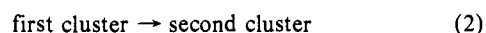
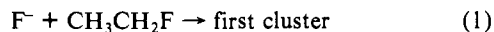
**Figure 1.** Energetics of the E2 reaction. *E* and *G* stand for the electronic and Gibbs free energies (298.15 K and 1 atm) calculated with the 3-21G+p basis set, respectively. Values in this figure are the energy differences between two stationary points and they are in kcal/mol. TS denotes the transition state. "Clust." is the cluster standing for the charge-dipole complex.



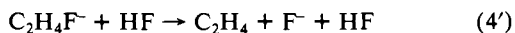
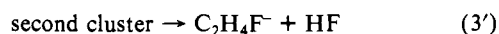
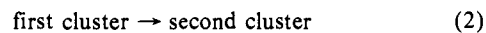
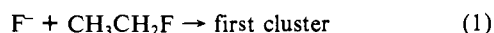
**Figure 2.** Energetics of the  $S_N2$  reaction. The same notations as in Figure 1 are used.

and  $FHF^-$  or into  $C_2H_4F^-$  and HF. The reaction schemes are represented in Schemes I and II. The elementary processes,

#### Scheme I



#### Scheme II



reactions 1 and 2, are common to Schemes I and II. The net E2 reaction is (2). The activation energy of (2) is calculated to be 28.7 kcal/mol in electronic energy and 25.5 kcal/mol in Gibbs free energy. The activation energies of (3) and (3') are not calculated here, because the second cluster is a loosely bound complex of  $F^-$ , HF, and  $C_2H_4$  and the dissociation step is not considered.

**Table I.** Thermochemistry of Reactions of  $F^-$  with Ethyl Fluoride<sup>a</sup>

process no.	energy change and entropy change			
	$\Delta E$	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$
1	16.5 (13.0)	16.3 (12.8)	-22.36	9.6 (6.1)
2	-15.2 (-13.0)	-12.7 (-10.5)	6.52	-10.8 (-8.6)
3	27.0 (25.0)	28.8 (26.8)	20.79	35.0 (33.0)
4	-50.8 (-43.4)	-50.9 (-43.5)	25.65	-43.3 (-35.9)
3'	-14.8 (-9.9)	-13.5 (-8.6)	27.78	-5.2 (-0.3)
4'	-9.0 (-8.4)	-8.6 (-8.0)	18.66	-3.1 (-2.5)
5	16.3 (13.6)	16.6 (13.9)	-24.42	9.3 (6.6)
1 $\alpha^b$	16.0	15.9	-22.21	9.2

process no.	activation energy and entropy			
	$\Delta E^*$	$\Delta H^{\circ*}$	$\Delta S^{\circ*}$	$\Delta G^{\circ*}$
2 (E2)	28.7 (28.1)	25.1 (24.5)	-1.39	25.5 (24.9)
6 ( $S_N2$ )	17.8 (23.6)	16.9 (22.7)	-4.49	18.3 (24.1)

<sup>a</sup>Energies (positive: exothermic) are in kcal/mol and entropies are in entropy units. Thermochemical quantities are at 298.15 K and 1 atm.  $\Delta E$  and  $\Delta E^*$  in parentheses were calculated by the DZ+p+p' basis set. The other values in parentheses were estimated on the basis of the vibrational analysis with the 3-21G+p basis set. <sup>b</sup>The formation of the  $\alpha$ -hydrogen attacked cluster.

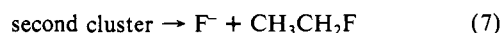
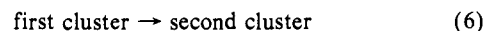
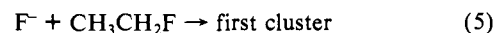
**Table II.** Activation Entropies,  $\Delta S^*$ , for E2 and  $S_N2$  Reactions<sup>a</sup>

reactions	solvent	$S_N2$	E2
<i>i</i> -PrBr + EtO <sup>-</sup>	60% EtOH	-17.5	-12.9
EtS <sup>+</sup> Me <sub>2</sub> + EtO <sup>-</sup>	100% EtOH	11.0	16.6
<i>n</i> -PrS <sup>+</sup> Me <sub>2</sub> + EtO <sup>-</sup>	100% EtOH	11.5	15.1
( $\alpha$ -phenylethyl)S <sup>+</sup> Me <sub>2</sub> + EtO <sup>-</sup>	100% EtOH	6.9	17.0

<sup>a</sup>These data are taken from ref 12.  $\Delta S^*$  is in entropy units.

The  $S_N2$  reaction scheme is found to be composed of three elementary processes. The energetics are shown in Figure 2. At the initial stage of the reaction,  $F^-$  approaches EtF from the backside of the  $\alpha$ -carbon, and the first cluster is formed. This first cluster is different from that of the E2 reaction. Then, the first cluster rearranges to the second cluster which is the same as the first cluster of the  $S_N2$  reaction. The second cluster decomposes into EtF and  $F^-$ . The  $S_N2$  reaction scheme is represented in Scheme III. The net  $S_N2$  reaction is (6), and its activation

#### Scheme III

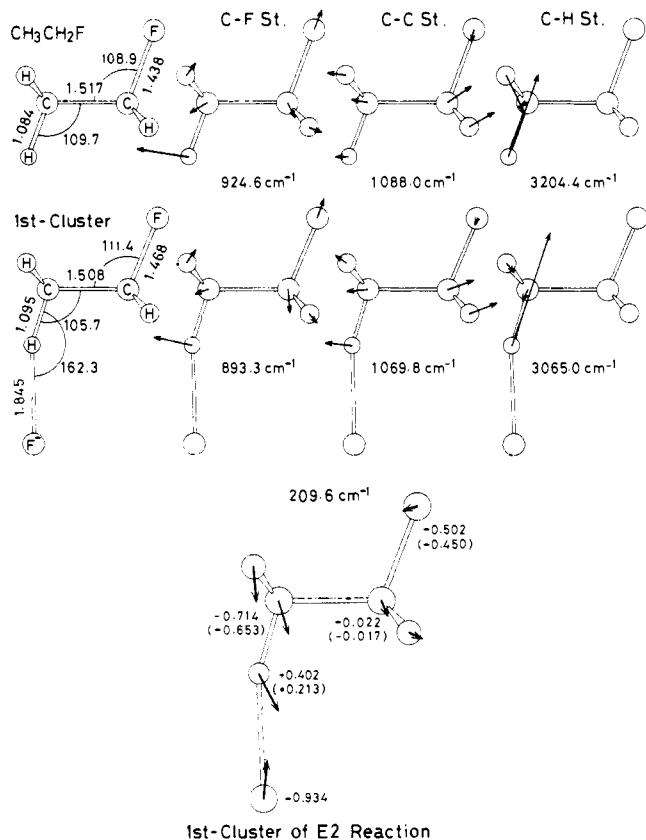


energy is calculated to be 17.8 kcal/mol in electronic energy and 18.3 kcal/mol in Gibbs free energy. It should be noted that the activation energy of the E2 reaction is larger than that of the  $S_N2$  reaction.

The thermochemistry of the elementary processes is summarized in Table I. Table I shows that the activation entropy,  $\Delta S^{\circ*}$ , of the net E2 reaction, (2), is larger than that of the net  $S_N2$  reaction, (6). This result is in agreement with the entropy changes estimated for the nucleophilic reactions in solution in Table II.<sup>12</sup> The entropy change is more favorable for the E2 reaction, which means that an increase in temperature increases the E2 proportion. An example is found in the ethoxide-induced elimination of ethyldimethylsulfonium ion. The elimination gives 14, 16, 20, and 21% ethylene at 35, 45, 64, and 73 °C, respectively.<sup>12a</sup> Therefore, it is an intrinsic nature of nucleophilic reactions that the activation entropy of the E2 reaction is larger than that of the  $S_N2$  reaction.

**Vibrational Analysis.** The first cluster of the E2 reaction is examined by vibrational analysis. Some vibrational modes and the structure of the first cluster are depicted in Figure 3 together with the corresponding ones of EtF. Various geometric distortions take place through the attachment of  $F^-$  to EtF, and those changes

(12) (a) Banthorpe, D. V.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* 1960, 4054. (b) Hughes, E. D.; Ingold, C. K. et al. *Ibid.* 1948, 2093.

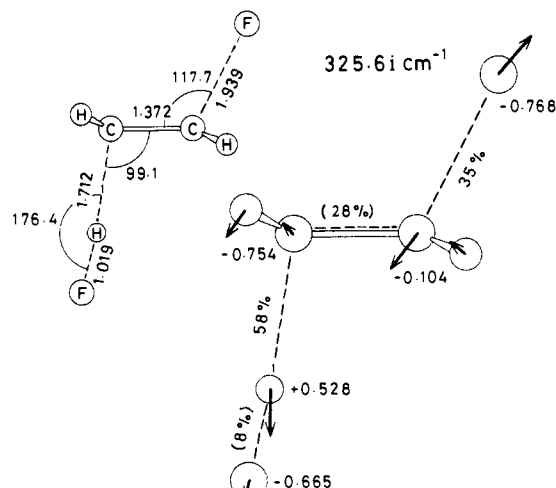


**Figure 3.** Geometries and vibrational modes of fluoroethane and the E2 first cluster. In the upper figures, bond lengths and angles are in angstroms and degrees, respectively. C-F St., C-C St., and C-H St. mean C-F stretch, C-C stretch, and C-H stretch modes, respectively. The lower figure shows the in-plane mode of the lowest frequency. Values in this figure show the net charges of the first cluster and those in parentheses are the net charges of fluoroethane.

are described clearly by the vibration frequencies. It is found that the vibrational frequencies of the C-H and C-F stretches are decreased ( $3204 \rightarrow 3065 \text{ cm}^{-1}$  and  $924 \rightarrow 893 \text{ cm}^{-1}$ ). This result indicates that the first cluster formation weakens the C-H bond and C-F bond, which is also shown in the elongation of these two bonds and C-F bonds. The analysis implies that scission of these two bonds is synchronous. Figure 3 shows the electron distribution in the first cluster. The electron density on F<sup>-</sup> begins to move toward the fluorine atom of EtF. At the initial stage of the E2 reaction, the vibrational mode of  $209.6\text{-cm}^{-1}$  frequency is a main component of the reaction coordinate because this mode has the F-H stretching character, as Figure 3 shows.

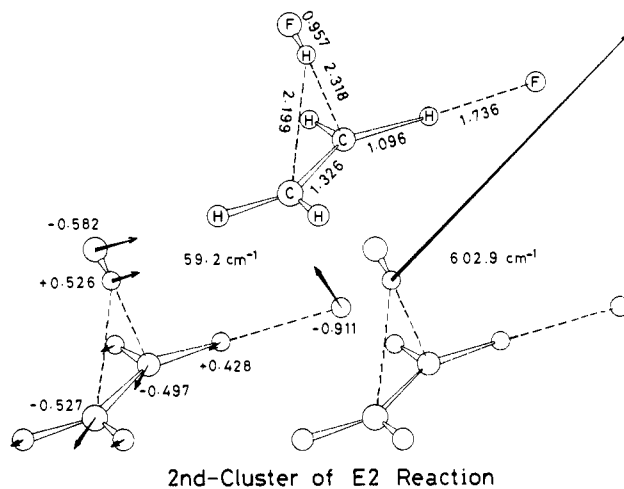
The vibrational analysis is made on the stationary point between the first cluster and the second cluster, and only one imaginary frequency,  $325.61 \text{ cm}^{-1}$ , is obtained. Thus, the stationary point is confirmed to be a transition state of the net E2 reaction, (2). The imaginary frequency mode is shown in Figure 4 together with the structure and charge distribution of the transition state. The analysis demonstrates that the C-H bond and C-F bond cleave almost simultaneously and the newly formed H-C bond is almost complete at the transition state. The increments of the lengths of the breaking C-H and C-F bonds are 58% and 35% of the original bond lengths of EtF, respectively. The H-F bond is just 8% longer than that of an HF molecule. The electron density on F<sup>-</sup> is conveyed to the  $\beta$ -carbon and leaving fluorine atoms, and the carbon atom has anionic character. The H-F part has only  $-0.137$  net charge ( $-0.665 + 0.528$ ).

Figure 5 presents the geometry and two low-frequency vibrational modes of the second cluster. It should be noted that Figure 5 is upside-down relative to Figures 3 and 4. The second cluster is a loosely bound complex of C<sub>2</sub>H<sub>4</sub>, HF, and F<sup>-</sup>, and the net E2 reaction, (2), terminates at the second cluster. The low-frequency modes indicate that the second cluster can decompose in two ways.



#### Transition State of E2 Reaction

**Figure 4.** Geometry and imaginary-frequency mode of the transition state of the net E2 reaction. Bond lengths and angles are in angstroms and degrees, respectively. Values on the atoms are the net charges. The increments of the bond lengths relative to those of fluoroethane are based on the C=C and H-F bond lengths of the products, ethylene and hydrogen fluoride. In the calculation of the C-C bond change, 0% means that the ethylenic C=C bond is completed, and 100% means that the C-C bond of EtF is not elongated at all.



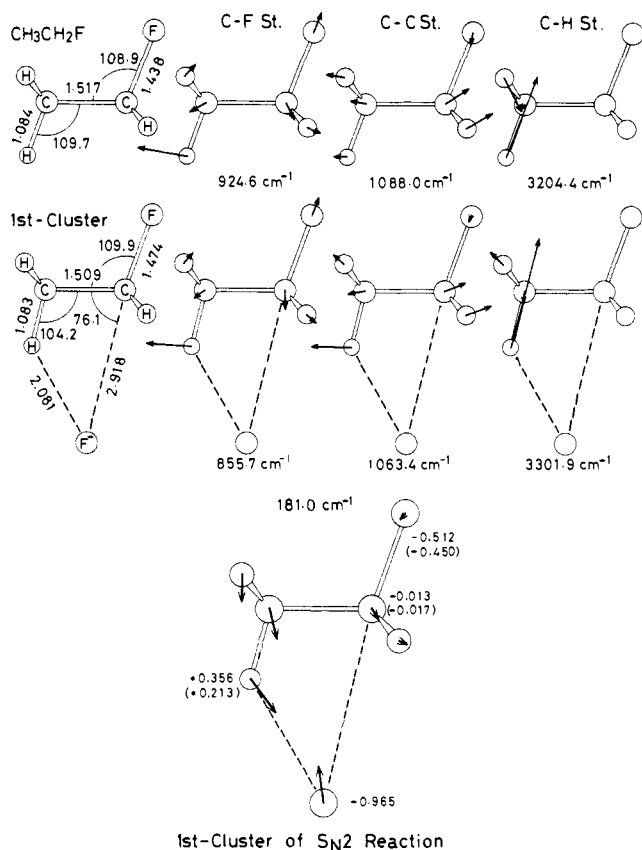
#### 2nd-Cluster of E2 Reaction

**Figure 5.** Geometry and low-frequency vibrational modes of the E2 second cluster. Bond lengths and angles are in angstroms and degrees, respectively. Values on the left side of the figure show the net charges.

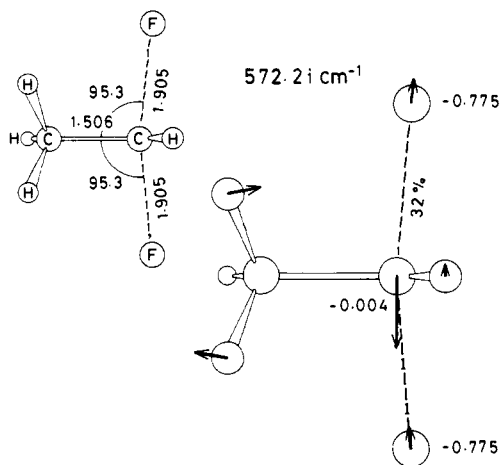
The mode of  $59.2 \text{ cm}^{-1}$  leads to C<sub>2</sub>H<sub>4</sub> and FHF<sup>-</sup>, and that of  $602.9 \text{ cm}^{-1}$  gives C<sub>2</sub>H<sub>4</sub>F<sup>-</sup> and HF. The former process occurs more readily than the latter, judging from the large difference in the frequencies. Indeed, this is shown by the energy difference between (3) and (3') in Figure 1.

The first cluster of the S<sub>N</sub>2 reaction is examined by vibrational analysis. The result is shown in Figure 6 together with its geometry and charge distribution. It is shown that the first cluster can proceed in two directions, toward the transition state of the S<sub>N</sub>2 reaction, (6), and toward the first cluster of the E2 reaction. In the first cluster of the S<sub>N</sub>2 reaction, the C-F bond begins to be weakened. However, the in-plane low-frequency vibrational mode,  $181.0 \text{ cm}^{-1}$ , is composed of the C-F<sup>-</sup> and H-F stretching modes, and the latter component is larger than the former. Therefore, this mode readily leads to the first cluster of the E2 reaction.

Figure 7 shows an imaginary frequency mode of the stationary point between the first and second clusters of the S<sub>N</sub>2 reaction. The vibrational analysis gives two imaginary frequencies for the stationary point,  $135.4i$  and  $572.2i \text{ cm}^{-1}$ . The former corresponds to a rotational mode of the methyl group. The latter is along the reaction coordinate as Figure 7 shows. Although the stationary



**Figure 6.** Geometry and vibrational modes of fluoroethane and the  $S_N2$  first cluster. The same notations as in Figure 3 are used.

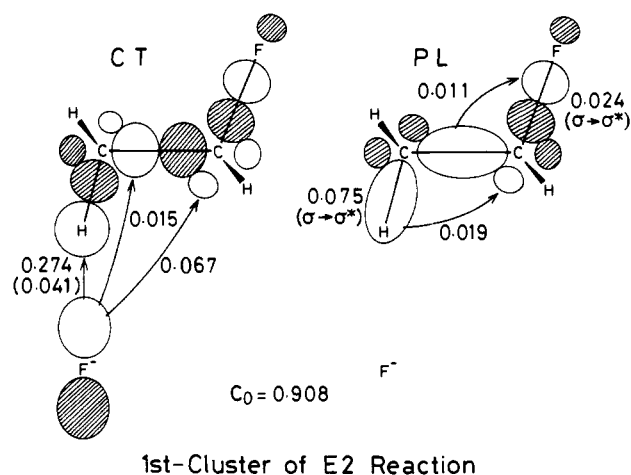


### Transition State of $S_N2$ Reaction

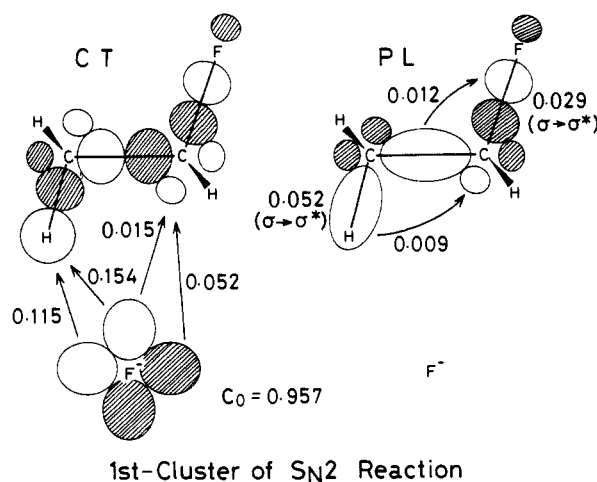
**Figure 7.** Geometry and vibrational mode along the reaction coordinate at the transition state of the net  $S_N2$  reaction. The same notations as in Figure 4 are used.

point has two imaginary frequencies, it is approximately regarded as the transition state of the  $S_N2$  reaction here. At the transition state, the increment of the breaking C-F bond is 32% of the C-F bond of EtF.

**Orbital Interaction.** The orbital interaction<sup>13</sup> in the first cluster of the E2 reaction is investigated by configuration analysis<sup>14</sup> in order to deduce the driving force for the E2 reaction. The wave function of the first cluster is expanded by the wave functions composed of the localized molecular orbitals (LMO's)<sup>15</sup> of  $F^-$  and



**Figure 8.** Schematic presentation of results of configuration analysis on the E2 first cluster. Values denote the coefficients of the electron configurations and  $C_0$  means the coefficient of the original adiabatic configuration. The value in parentheses shows a two-electron-transfer configuration.



**Figure 9.** Schematic presentation of results of configuration analysis on the  $S_N2$  first cluster. The same notations as in Figure 8 are used.

EtF. The result is schematically presented in Figure 8. The origin of the weakening of the C-H bond is shown to be the charge-transfer interactions (CT's) from the lone-pair orbital of  $F^-$  to the unoccupied C-H bond orbital (0.274 and 0.041). The weakening of the C-F bond is caused by CT from the lone-pair orbital of  $F^-$  to the unoccupied C-F bond orbital (0.067). The polarization interactions (PL's) from the C-H and C-F bond orbitals to the unoccupied C-F bond orbital also work for the C-F bond weakening. Since PL's are induced by the mixing-in of the C-H bond orbitals with the C-F bond orbitals through the  $F^-$  lone-pair orbital, the concerted E2 reaction requires the coplanarity of the C-H and C-F bonds.<sup>6a</sup>

The wave function of the first cluster of the  $S_N2$  reaction is expanded by the LMO wave functions of  $F^-$  and EtF. The result is shown in Figure 9. CT's from the  $F^-$  lone-pair orbitals to the unoccupied C-F bond orbital weaken the C-F bond. Large components (0.154 and 0.115) of the wave function of the first cluster are CT's from the  $F^-$  lone-pair orbitals to the unoccupied C-H bond orbital. This means that the interaction between  $F^-$  and the  $\beta$ -hydrogen is larger than that between  $F^-$  and the  $\alpha$ -carbon. Thus, the first cluster of the  $S_N2$  reaction tends to isomerize readily to the first cluster of the E2 reaction.

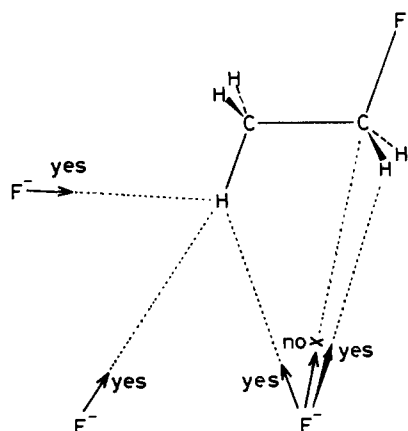
**E2 Reaction vs.  $S_N2$  Reaction.** The E2 reaction occurs exclusively in the gas phase.<sup>7,16</sup> However, the activation energy of the net E2 reaction is calculated to be larger than that of the  $S_N2$

(13) Fukui, K. "Theory of Orientation and Stereoselection"; Springer-Verlag: Heidelberg, 1970.

(14) (a) Fujimoto, H.; Kato, S.; Yamabe, S.; Fukui, K. *J. Chem. Phys.* **1974**, *60*, 572. (b) Baba, H.; Suzuki, S.; Takemura, T. *Ibid.* **1969**, *50*, 2078.

(15) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457.

reaction or almost the same as Table I shows. Why does the E2 reaction occur exclusively in the gas phase? Another cluster in which an  $\alpha$ -hydrogen is attacked by F<sup>-</sup> is calculated, and it is found that its total energy is almost the same as that of the first cluster of the S<sub>N</sub>2 reaction, and therefore it is also readily formed in the gas phase. That is, when F<sup>-</sup> approaches EtF, F<sup>-</sup> has three kinds of targets,  $\alpha$ -hydrogen,  $\beta$ -hydrogen, and  $\alpha$ -carbon. When the geometry of EtF is taken into account, the  $\alpha$ -carbon is as small as a pin-point for the attacking F<sup>-</sup> as the following figure shows.



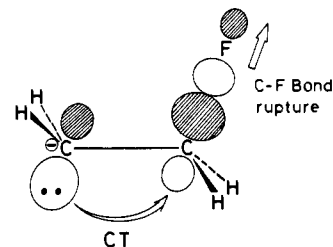
Therefore, the approach of F<sup>-</sup> to EtF usually gives the first cluster of the E2 reaction or the cluster in which the  $\alpha$ -hydrogen is attacked. Even if the first cluster of the S<sub>N</sub>2 reaction were formed, this cluster would be converted to the first cluster of the E2 reaction. Indeed, the vibrational and configurational analyses have shown this result. This collisional preference reflects the favorableness of the E2 reaction in the gas phase.

Recently, the contrary result was obtained in the gas-phase reaction of Cl<sup>-</sup> with bromoethane by Kebarle et al.<sup>17</sup> The ionic product, ClHBr<sup>-</sup>, was not detected in the reaction. The finding demonstrates that only the S<sub>N</sub>2 channel is possible in the gas-phase reaction of Cl<sup>-</sup> with bromoethane. That is, the S<sub>N</sub>2/E2 proportion in the reaction of Cl<sup>-</sup> with bromoethane is opposite to that in the reaction of F<sup>-</sup> with EtF. This may arise from differences of the ion radius and basicity of the reagents. This point will be discussed in our subsequent paper.<sup>18</sup>

In solution the S<sub>N</sub>2 reaction competes with the E2 reaction, and the latter is usually minor. This is elucidated as follows. In solution, the  $\alpha$ - and  $\beta$ -hydrogens are very good targets for solvent molecules as they are good targets for F<sup>-</sup> in the gas phase. Solvation of  $\beta$ -hydrogens will block the formation of the first cluster leading to the E2 reaction. Therefore, a base attacks the  $\alpha$ -carbon, and the S<sub>N</sub>2 reaction can occur in solution. This solvation determines the reactivity of the E2 reaction in solution. The E2 proportion depends upon the strength of the bases used and the polarity of the solvents. An increase of the base strength usually enhances the E2 reaction, and a decrease of the solvent polarity increases its proportion. When the base is strong and/or the solvent polarity is small, an attacking base can break the hydrogen bond between the  $\beta$ -hydrogen and solvent molecules and it readily attacks the  $\beta$ -hydrogen. Then, the E2 reaction proceeds. The intrinsic large reactivity of the  $\beta$ -hydrogens of substrates makes the possibility of the E2 reaction small, and it makes the S<sub>N</sub>2 reaction major in polar solution.

**Possibility of E1cB Mechanism.** The present computational results indicate that the F<sup>-</sup>-induced elimination of EtF proceeds in a concerted manner. The nonconcerted process corresponds to the E1cB mechanism. In this mechanism, the attacking F<sup>-</sup>

abstracts a  $\beta$ -proton from EtF, and then the F<sup>-</sup> leaves. The possibility of this mechanism depends on the stability of the intermediate, 2-fluoroethyl anion. This species was examined by Schleyer et al. together with various substituted ethyl anions.<sup>19</sup> According to their calculation, the 2-fluoroethyl anion is not present and only a loosely bound complex of H<sub>2</sub>C=CH<sub>2</sub>...F<sup>-</sup> is formed. The absence of 2-fluoroethyl anion is ascribed to the hyperconjugation (CT from the lone pair of 1-carbon to the unoccupied C-F bond orbital).



Thus, it is confirmed that the E1cB mechanism is unlikely. However, if electron-withdrawing groups are introduced into the substrates, the intermediate anion may be present.<sup>19</sup> In this case, the power of CT is weakened by the electron shift from the lone pair of the anion to the substituents.

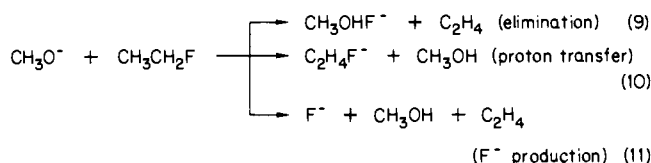
#### Comparison with Published Experimental Data

Since the gas-phase reaction of F<sup>-</sup> with EtF is observed,<sup>7</sup> the results calculated here can be compared with the experimental results. The reaction of F<sup>-</sup> with EtF is reported to lead exclusively to the elimination of HF and formation of FHF<sup>-</sup>. This result



is in line with the calculated results. Although the reaction of F<sup>-</sup> with EtF is shown to proceed in two ways, Schemes I and II, Scheme I is energetically favored. The last step of Scheme I, (4), does not occur because the F<sup>-</sup> binding energy to HF is sufficiently large.<sup>20</sup>

When the attacking base is CH<sub>3</sub>O<sup>-</sup>, three reaction channels are observed.



This observation is explained by the energetics calculated here. Reactions 9 and 10 correspond to (1) → (2) → (3) and (1) → (2) → (3') in the F<sup>-</sup> case, respectively. In the case of CH<sub>3</sub>O<sup>-</sup>, a (3')-type reaction can occur, while reaction 3' does not occur in the case of F<sup>-</sup>. This difference may come from differences in the hydrogen bond strengths between CH<sub>3</sub>OH and HF. HF forms a stronger hydrogen bond than CH<sub>3</sub>OH. For example, the hydrogen bond energy of HF and F<sup>-</sup> is 39 kcal/mol,<sup>20</sup> and that of CH<sub>3</sub>OH and F<sup>-</sup> is 29.6 kcal/mol.<sup>21</sup> Reaction 11 corresponds to Scheme II, (1) → (2) → (3') → (4'). The ion C<sub>2</sub>H<sub>4</sub>F<sup>-</sup> formed in (10) separates into C<sub>2</sub>H<sub>4</sub> and F<sup>-</sup>, because the hydrogen bond of C<sub>2</sub>H<sub>4</sub>...F<sup>-</sup> is weaker than that of CH<sub>3</sub>OH...F<sup>-</sup>.<sup>7b</sup>

Substituent effects have been reported for the reaction of CD<sub>3</sub>O<sup>-</sup> with fluoroethanes. The results are summarized in Table III,<sup>7a</sup> which shows that the ratio of elimination to proton transfer depends on the position of the substituents. Substitution on the  $\alpha$ -carbon makes elimination favorable, while substitution on the  $\beta$ -carbon makes proton transfer favorable. The mechanism of the reaction of  $\alpha$ -substituted fluoroethanes is different from that of  $\beta$ -substituted fluoroethanes. In the case of  $\alpha$ -substitution, the

(16) (a) DePuy, C. H.; Blerbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034. (b) King, G. K.; Marioq, M. M.; Blerbaum, V. M.; DePuy, C. H. *Ibid.* **1981**, *103*, 7133.

(17) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959.

(18) In our preliminary calculation of the reaction of Cl<sup>-</sup> with chloroethane, the Cl<sup>-</sup> was found to form only the first cluster for the S<sub>N</sub>2 reaction. To be published.

(19) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141. See also: Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221.

(20) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 5848.

(21) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944.

**Table III.** Proportion of Elimination and Proton Transfer of  $\text{CD}_3\text{O}^-$  and Fluoroethanes<sup>a</sup>

reaction	% of elimination	% of proton transfer	mechanism
$\text{CD}_3\text{O}^- + \text{CH}_3\text{CH}_2\text{F}^b$	29	71	E2
$\text{CD}_3\text{O}^- + \text{CH}_3\text{CHF}_2$	71	29	E2, E1cB
$\text{CD}_3\text{O}^- + \text{CH}_3\text{CF}_3$	93	7	E2, E1cB
$\text{CD}_3\text{O}^- + \text{CH}_3\text{CHF}_2$	71	29	E2, E1cB
$\text{CD}_3\text{O}^- + \text{CH}_2\text{FCHF}_2^b$	50	50	E2, E1cB
$\text{CD}_3\text{O}^- + \text{CHF}_2\text{CHF}_2$	11	89	E2, E1cB
$\text{CD}_3\text{O}^- + \text{CH}_3\text{CF}_3$	93	7	E2, E1cB
$\text{CD}_3\text{O}^- + \text{CH}_2\text{FCF}_3$	61	39	E2, E1cB
$\text{CD}_3\text{O}^- + \text{CHF}_2\text{CF}_3$	0	100	E1cB

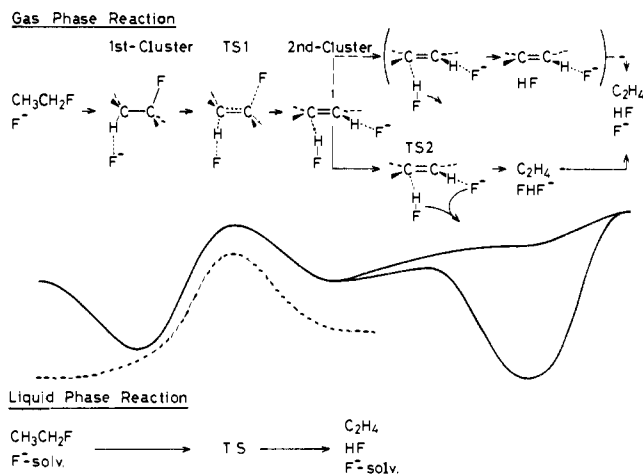
<sup>a</sup>These data are taken from ref 7a. <sup>b</sup>The  $\text{F}^-$  production, reaction 11, is added to the proton transfer.

possibility of forming the second cluster is small, due to the decrease in the number of  $\alpha$ -hydrogens which are the targets for the leaving  $\text{F}^-$  (see Figure 5). Therefore,  $\text{F}^-$  leaves with  $\text{CH}_3\text{OH}$  without forming the second cluster; the elimination proportion becomes large. In this respect, it seems strange that 1,1,1-trifluoroethane, without any  $\alpha$ -hydrogens, gives proton transfer (7%). This proton transfer must occur either through the  $\beta$ -hydrogen-attacked second cluster (in which the  $\beta$ -hydrogen is attacked) or by a E1cB mechanism, the possibility of which was suggested in the previous section. On the other hand, in the case of the  $\beta$ -substitution the E1cB mechanism is dominant. The more substituted fluoroethanes favor the E1cB mechanism. Therefore, the reaction of  $\text{CH}_3\text{O}^-$  with  $\beta$ -substituted fluoroethanes proceeds via the E1cB mechanism, and the preference of proton transfer for the  $\beta$ -substituted fluoroethanes is understandable.

### Concluding Remarks

In the present work, the gas-phase reactions of  $\text{F}^-$  with EtF are investigated by ab initio calculations. The E2 reaction is represented by four elementary processes, first cluster formation, net E2 reaction forming the second cluster, decomposition of the second cluster, and production of  $\text{C}_2\text{H}_4$ ,  $\text{F}^-$ , and HF. Two routes are found in the decomposition of the second cluster. The result is schematically presented in Figure 10. When the attacking base is  $\text{F}^-$ , only the decomposition route giving  $\text{C}_2\text{H}_4$  and  $\text{FHF}^-$  is possible. On the other hand, both routes are possible in the case of  $\text{CH}_3\text{O}^-$  attack. In the net E2 reaction, scission of the C-H bond and C-F bond is synchronous. The E1cB mechanism is improbable in this case, because the intermediate, 2-fluoroethyl anion, is unstable.

Although the potential energy profile of the E2 reaction in solution is not traced here, it is deduced from the potential energy profile of the gas-phase reaction on the basis of Jorgensen's result.<sup>22</sup>



**Figure 10.** Summary of the E2 reaction of  $\text{F}^-$  with ethyl fluoride. " $\text{F}^-$ -solv." means the solvated fluoride anion.

The energetics of the  $\text{S}_{\text{N}}2$  reaction of  $\text{Cl}^-$  with chloromethane in aqueous media has been correctly estimated by the use of a theoretical calculation by Jorgensen et al. The difference in the energy profiles between the gas phase and aqueous phase has been quantitatively reproduced by Monte Carlo simulation for the reaction system and 250 water molecules. Solvation has been found to lead to a flattening of the ion-dipole minima and to an increase in the free energy of activation. Our predicted energy profile for the E2 reaction is shown by the bold broken line in Figure 10. In solution the first cluster formation is veiled by solvation of the attacking base. The second cluster is not formed in solution. The leaving group is solvated, and it goes away without forming the second cluster. Thus, in solution the potential energy profile of the concerted E2 reaction is represented by a single-maximum curve.

The  $\text{S}_{\text{N}}2$  reaction in the gas phase is found to be composed of three elementary processes, first cluster formation, net  $\text{S}_{\text{N}}2$  reaction forming the second cluster, and decomposition of the second cluster. The first cluster of the  $\text{S}_{\text{N}}2$  reaction is different from that of the E2 reaction. Comparison of the E2 reaction with the  $\text{S}_{\text{N}}2$  reaction reveals the preference of the former in the gas phase. On the other hand, the  $\text{S}_{\text{N}}2$  reaction is usually a major reaction because of the solvation phenomenon which diminishes the collision cross section of the E2 reaction.

**Acknowledgment.** The authors thank the Institute for Molecular Science for the allotment of the CPU time of the HITAC M-200H computer. The program package of the vibrational analysis has been coded by Dr. K. Yamashita, to whom they are grateful. The authors also acknowledge the referees for their useful comments and refinement of English.

**Registry No.**  $\text{F}^-$ , 16984-48-8; fluoroethane, 353-36-6.

(22) Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 3049.