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REACTION OF METHANE WITH MOLECULAR FLUORINE: AN *AB INITIO* MO STUDY1)

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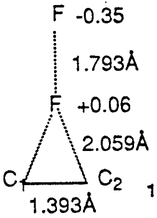
The whole process for the substitution of C-H bond in methane with fluorine by molecular fluorine was analyzed at HF/6-311++G** level with IRC calculation. Theoretical information including the transition state of this reaction was obtained in regard to electrophilic nature and retention of configuration.

KEYWORDS fluorination; molecular fluorine; HF/6-311++G**; intrinsic reaction coordinate; pentacoordinated carbonium ion; electrophilic front side attack

Solution of flourine diluted with inert gases (N_2 or Ar) provides controllable and selective reactions, and synthetic applications have greatly increased with the commercial availability of these diluted solutions.2) Among such reactions, the substitution of C-H in alkanes and the addition to C=C bonds in alkenes are two major reactions. Previously, we have demonstrated by MO calculation (MP2/6-31+G) that *syn* addition of fluorine to C=C bond is an electrophilic process and proceeds *via* the perpendicular π-complex (**1**) followed by the transformation to the species (**2**) as the transition state.3,4)

In continuation of our mechanistic studies on the use of elemental fluorine as the fluorinating reagent, we were interested in extending our investigation to the fluorination of C-H bond in alkanes. In this paper, we present the result.



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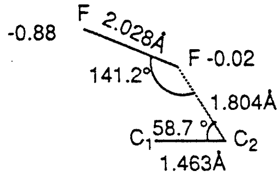

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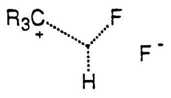


3

Accumulated experimental data show that elemental fluorine under suitable conditions can replace unreactive hydrogen in various aliphatic compounds with great regio- and stereoselectivities. Thus, the reactivity is in the order of R_3C-H > R_2HC-H > RH_2C-H5) and stereoselectivity is in a full retention.6) To our knowledge, explanation for these selectivities has only been proposed in terms of electronic theory by Rozen and his collaborators.5,6) They proposed the following mechanism including **3** as the intermediate or transition state. A similar pentacoordinated carbonium ion for electrophilic attack of H^+ or D^+ on C-H was first proposed by Olah *et al.*7) and later extended to an insertion of OH^+8) or O_3H^+9) into the C-H bonds. Though such species could account well for the electrophilic nature and stereoselectivity (retention of configuration), it is uncertain whether **3** is the transition state or the intermediate, and its exact characterization (*i.e.* arrangement of the composed atoms, charges, *etc.*) has not been provided. It is therefore meaningful to analyze more quantitatively the whole process by MO theory.

When *ab initio* calculation using methane as the substrate was carried out at the Hatree-Fock level with the 6-311++G** basis set10) using the GAUSSIAN92 system of programs,11) the complex (**6**) was deduced to be a suitable transition state. Its structure was fully optimized and confirmed to have single imaginary frequency. In order to elucidate the whole process, the reaction path was traced from **6** to the reactants (CH_4 and F_2) and to the products (CH_3F and HF) by use of the IRC (intrinsic reaction coordinate) calculation.12,13) The result obtained is shown in Fig. 1, with essential parameters in Table I.

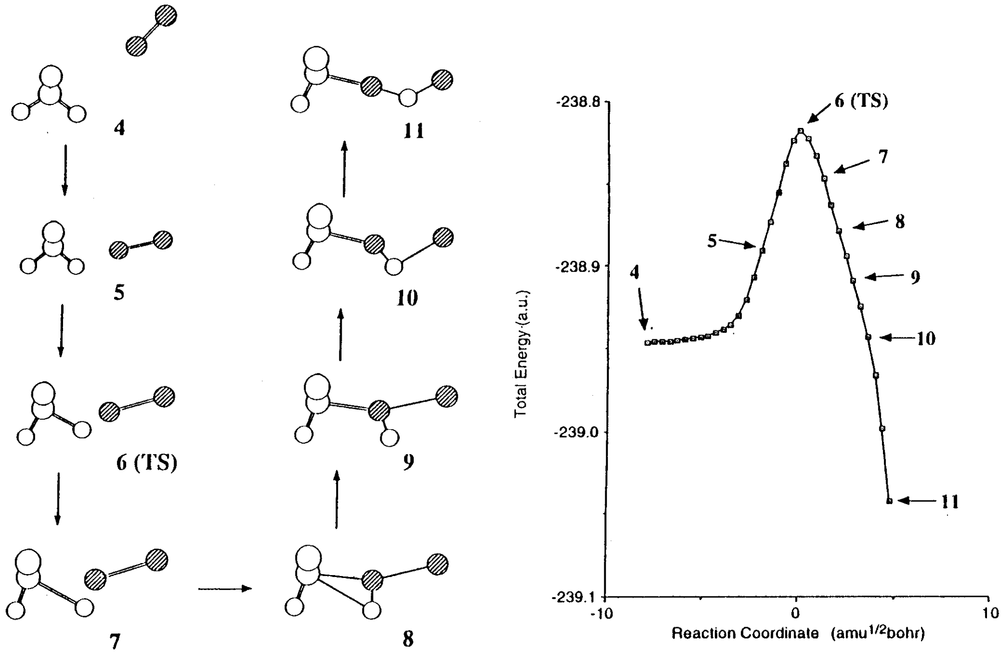


Fig. 1. Optimized Geometries and Potential Energy Profile along the Reaction Coordinate for the Substitution of CH_4 to CH_3F by F_2 (HF/6-311++G**)

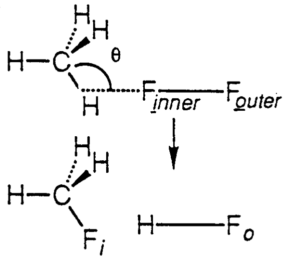
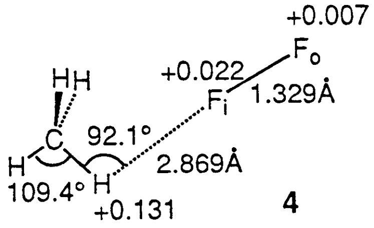


Table I. Energies, Distances, Angles, and Charges of the Interacting Species of F_2 and CH_4

Species	E (a.u)	Distance (Å) C-H	Distance (Å) C-F_i	Distance (Å) F_i-F_o	Angle (θ)	Charge F_i	Charge F_o
Reactant [a)] (CH_4)	-40.20915	1.084	∞	1.329	-	0	0
4	-238.94633	1.084	3.105	1.329	94°	+0.022	+0.007
5	-238.89073	1.074	2.261	1.546	125°	+0.116	-0.111
TS (6)	-238.81836	1.430	2.088	1.813	134°	+0.134	-0.555
8	-238.87896	2.222	1.935	2.001	136°	-0.004	-0.889
10	-238.94293	2.598	1.775	2.123	148°	-0.123	-0.880
Product [b)](CH_3F)	-139.08322	∞	1.366	∞	-	-0.238	-0.295

a) For F_2: E = -198.73728 a.u. b) For HF: E = -100.05331 a.u., $d_{H\text{-}F}$ = 0.897 Å.

In order to make the following discussion more clear, full data on three species (**4**, **6** and **8**) are also shown. As evidenced from the large negative charge of the outer fluorine (F_o) in the transition state (**6**), the reaction is surely electrophilic in nature. At the initial stage of the reaction, however, a slight reverse electron flow ($F_2 \rightarrow CH_4$) is found. It seems to be worthwhile to consider not only why such an electron shift occurs, but also the origin of the specified geometries in each stage. For the transition state (**6**) and its later species (*e.g.* **8**), geometry is similar to that (**A**) of CH_5^+ previously obtained from *ab initio* calculation.[14)] Obviously, **6**, **8** and **A** are isoelectronic with H_3^+ (**B**). In contrast, CH_5^- is calculated to have trigonal bipyramidal structure (**D**) which is isoelectronic with H_3^- (**E**). It is now well accepted that the electron-deficient two-electron-three center bonding system prefers a closed arrangement and hence relates to a front side electrophilic attack (**C**), while electron-rich four-electron-three center bonding adopts an open geometry and bears a close resemblance to the transition state (**F**) of nucleophilic attack on a tetrahedral carbon center.[15)]



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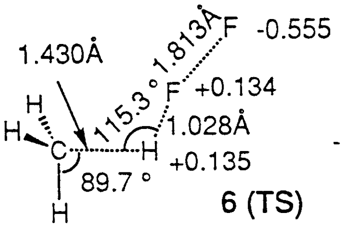
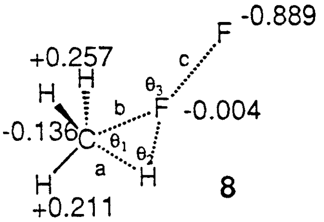


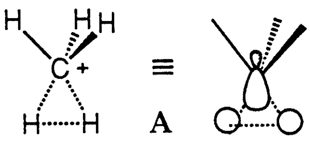
6 (TS)



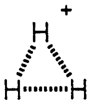
8

a	2.222
b	1.935
c	2.001
θ1	23.9
θ2	60.0
θ3	159.9

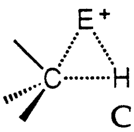
For analyzing the initial stage of the present reaction, HOMO-LUMO theory is especially suitable. With knowledge of the geometries (cf. **G**) at the initial stage, two interactions (**G-1** and **G-2**) are expected. The charge distribution of **4** indicates that the contribution of **G-1** [σ^*_{CH} (LUMO) - π^*_{F2} (HOMO)] is larger than that of **G-2** [σ_{CH} (HOMO) - σ^*_{F2} (LUMO)], which is responsible for the transition state (**6**) and its later species (*e.g.* **8**). This interpretation is in



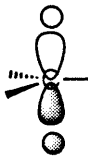
A



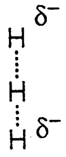
B



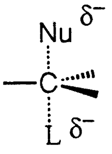
C



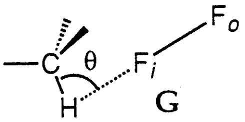
D



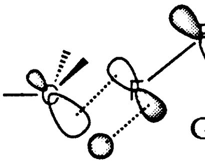
E



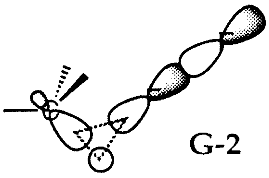
F



G



G-1



G-2

accordance with the angle (θ) between the C-H bond and the F - F axis in the corresponding species (**4**, **5**, and **6**), because interaction **G-1** should be the largest at 90° and the smallest at either 0° or 180°.

In summary, the following path was deduced for the front side attack of F_2 to the C-H bond of methane. First, F_2 approaches vertically (θ = *ca.* 90°) to the C-H bond. Then, fluorine shifts sideways to the C-H bond to give transition state **6**, whose θ is 134°. The former corresponds to interaction **G-1** and the latter to interaction **G-2**. Therefore, it can be concluded that the substitution of C-H of methane to C-F by F_2 should be categorized as an electrophilic reaction. Considering the energy gap of the corresponding frontier MOs, an energy-rich C-H bond should react preferentially (which has been verified experimentally), in good accordance with the present study.

REFERENCES AND NOTES

1) Cycloadditions in Synthesis. Part 65. For Part 64, see reference 3a.

2) S. T. Purrington, B. S. Kagen, *Chem. Rev.*, **86**, 997 (1986); S. Rozen, *Acc. Chem. Res.*, **21**, 307 (1988).

3) a) T. Iwaoka, C. Kaneko, A. Shigihara, H. Ichikawa, J. *Phys. Org. Chem.*, **6**, 195 (1993); b) T. Iwaoka, C. Kaneko, H. Ichikawa, *Chem. Pharm. Bull.*, **40**, 1969 (1992).

4) It should be noted that HOMO of F_2 is π^* and LUMO is σ^*. See for more detailed discussion: C. Kaneko, A. Toyota, J. Chiba, *Yakugaku Zasshi*, **114**, 160 (1994).

5) S. Rozen, C. Gal, *J. Org. Chem.*, **52**, 4928 (1987).

6) S. Rozen, C. Gal, *J. Org. Chem.*, **52**, 2769 (1987).

7) G. A. Olah, Y. Halpern, Y. Shen, Y. K. Mo, *J. Am. Chem. Soc.*, **95**, 4960 (1973).

8) G. A. Olah, N. Yoneda, D. G. Parker, *J. Am. Chem. Soc.*, **99**, 483 (1977).

9) G. A. Olah, N. Yoneda, D. G. Parker, *J. Am. Chem. Soc.*, **98**, 5261 (1976).

10) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980); M. J. Frish, J. A. Pople, *ibid.*, **80**, 3265 (1984).

11) M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, J. A. Pople, Gaussian 92, Revision B (IBM RS6000/550) Gaussian, Pittsburgh PA (1990).

12) K. Fukui, *J. Phys. Chem.*, **74**, 4161 (1970). See also, K. Fukui, S. Kato, H. Fujimoto, *J. Am. Chem. Soc.*, **97**, 1 (1975).

13) Algorithm developed by Gonzalez *et al.* C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.*, **90**, 2154 (1989); *idem*, *ibid.*, **94**, 5523 (1990).

14) J. B. Collins, P. v. Schleyer, J. S. Binkley, J. A. Pople, L. Radom, *J. Am. Chem. Soc.*, **98**, 3436 (1976); K. Raghavachari, R. A. Whiteside, J. A. Pople, P. v. Schleyer, *ibid.*, **103**, 5646 (1981). See also, A. Komornicki, D. A. Dixon, *J. Chem. Phys.*, **86**, 5625 (1987).

15) T. A. Albright, J. K. Bundett, M. -H. Whangbo, "Orbital Interactions in Chemistry," John-Wiley & Sons, N. Y., 1985.

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