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INDO STUDY OF 1,2-FLUORINE ATOM MIGRATION IN 1,2-DIFLUOROETHYL AND 1,1,2-TRIFLUOROETHYL RADICALS

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SUMMARY

INDO molecular orbital calculations have been carried out to estimate the barrier heights to the 1,2-migration of fluorine and hydrogen atoms in 1,2-difluoroethyl and 1,1,2-trifluoroethyl radicals. The calculated results suggest that (1) the 1,2-fluorine atom migration through a fluorine atom bridging intermediate will occur more readily than the 1,2-hydrogen atom migration through a hydrogen atom bridging intermediate in both radicals, (2) a fluorine atom will undergo 1,2-migration in 1,1,2-trifluoroethyl radical more readily than in 1,2-difluoroethyl radical. The enthalpy change accompanied by the 1,2-fluorine atom migration in 1,1,2-trifluoroethyl radical was estimated to be 1.7 kcal/mol, which was in good agreement with the value(1.6 kcal/mol) obtained experimentally.

INTRODUCTION

Experimentally, intramolecular 1,2-migration of chlorine or bromine atom has been found to occur in various chemical species[1-4]; however, the evidence for the 1,2-migration of

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fluorine atom is limited[5,6]. Siefert et al. investigated the reactions of recoil tritium atoms with cis- and trans-difluoroethylene and found that CF_2=CHT was one of the main products[7]. In the course of the formation of this product, 1,2-migration of fluorine atom may have to occur. Recently, our Laboratory has also studied the reactions of recoil tritium atoms with vinyl fluoride, 1,1-difluoroethylene, and trifluoroethylene, and obtained some evidence for the 1,2-fluorine atom migration in the 1,1,2-trifluoroethyl radical which was expected to be formed by the addition reaction of a tritium atom to trifluoroethylene[8].

In order to confirm this 1,2-fluorine atom migration in the 1,1,2-trifluoroethyl radical, we have made another experiment: the reaction of hydrogen atoms with trifluoroethylene using the mercury photosensitized decomposition of hydrogen as the source of hydrogen atoms[9]. The analysis of products was made by means of gas chromatography, mass spectrometry, and ^{1}H- and ^{19}F-NMR spectroscopy. Main products observed were CF_3CH_3, $CF_3CH_2CH_2CF_3$, $CF_3CH_2CF_2CH_2F$, $CF_3CH_2CHFCHF_2$, $CH_2FCF_2CF_2CH_2F$, and $CH_2FCF_2CHFCHF_2$. Since the radicals expected to be formed in the reaction between hydrogen atoms and trifluoroethylene are CF_2CH_2F and CHF_2CHF, the first four main products observed which contain CF_3CH_2- group, cannot be expected to be formed, if 1,2-fluorine atom migration does not occur in the radicals primarily produced.

Thus, we could experimentally confirm the 1,2-fluorine atom migration in the trifluoroethyl radical produced by the addition of hydrogen atom to trifluoroethylene; however, it is known that 1,2-hydrogen atom migration does not occur in the ethyl radical produced by the addition of hydrogen atom to ethylene[1]. Moreover, the binding energy of the C-F bond is a little larger than that of the C-H bond in fluorinated hydrocarbons. This apparent inconsistency prompted us to examine the theoretical approach to these intramolecular migrations.

There have been a number of molecular orbital calculations on the barriers to the 1,2-migrations of hydrogen and chlorine atoms through the bridged intermediates[10-13]. The 1,2-fluorine atom migration, however, has been studied only for monofluoroethyl radical[13,14]. The calculated barrier heights ranged from 28.6 to 107 kcal/mol depending upon the methods used.

The objective of the present work is to theoretically estimate the barrier heights to the 1,2-migration of fluorine and hydrogen atoms in 1,2-difluoroethyl and 1,1,2-trifluoroethyl radicals and confirm the experimental results described above.

CALCULATIONS

Total energies and geometries of open and bridged structures of ethyl, difluoroethyl, and trifluoroethyl radicals were determined by the INDO molecular orbital calculations. For ethyl type radicals, methyl group structures were assumed to be the same as those in corresponding fluorinated ethanes, and for bridged radicals, a bridging atom was assumed to occupy the position at the top of the isosceles triangle made of the C-C bond as one side.

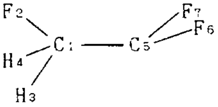
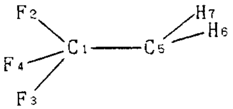
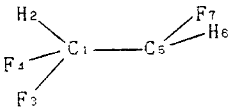
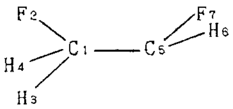
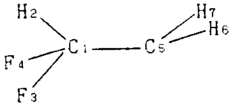
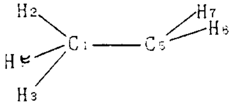
The INDO calculation was performed with the same parametrization as the Pople original version. The program was incorporated with the automatic geometry optimization based on the Davidon-Fletcher-Powell(DFP) algorithm. The descent direction in each cycle of optimization was determined by Broyden-Fletcher-Goldfarb-Sanno(BFGS) modification, which provides good stability and rapid convergence around the optimum point.

RESULTS AND DISCUSSION

The geometries of optimized structures of ethyl, difluoroethyl, and trifluoroethyl radicals are shown in Table 1. For the bridged structures in which the bridging atom is constrained at the top of the isosceles triangle made of the C-C bond as one side, the geometries optimized are shown in Table 2, in which 6 bond lengths and 11 bond angles are variables. Total energies calculated for these radicals are summarized in Table 3. Table 4 summarizes total energies of stable ethylene, fluorinated ethylenes, and hydrogen and fluorine atoms calculated by the INDO.

TABLE 1

Optimized Geometries for Open- Structures of Trifluoroethyl, Difluoroethyl, and Ethyl Radicals

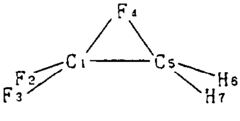
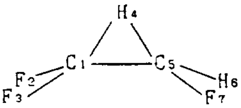
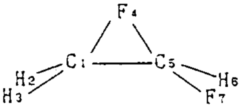
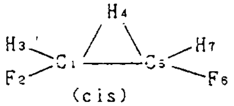
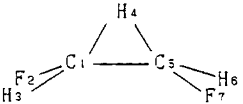
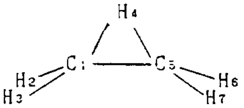
Chemical Species	Geometry		
	r(C1F2)=1.389 r(C1H3)=1.103 r(C1H4)=1.103 r(C1C5)=1.435 r(C5F6)=1.332 r(C5F7)=1.333	∠ F2C1H3=108.3 ∠ H3C1H4=107.9 ∠ H4C1F2=108.3 ∠ C5C1F2=110.3 ∠ C5C1H3=111.0 ∠ C5C1H4=111.0	∠ F6C5F7=108.7 ∠ C1C5F6=125.9 ∠ C1C5F7=125.4
	r(C1F2)=1.340 r(C1F3)=1.340 r(C1F4)=1.340 r(C1C5)=1.449 r(C5H6)=1.109 r(C5H7)=1.110	∠ F2C1F3=106.9 ∠ F2C1F4=106.9 ∠ F4C1F2=106.9 ∠ C5C1F2=111.9 ∠ C5C1F3=111.9 ∠ C5C1F4=111.9	∠ H6C5H7=116.4 ∠ C1C5H6=121.9 ∠ C1C5H7=121.7
	r(C1H2)=1.081 r(C1F3)=1.364 r(C1F4)=1.364 r(C1C5)=1.448 r(C5H6)=1.112 r(C5F7)=1.332	∠ H2C1F3=108.5 ∠ F3C1F4=107.3 ∠ F4C1H2=108.5 ∠ C5C1H2=111.0 ∠ C5C1F3=110.7 ∠ C5C1F4=110.7	∠ H6C5F7=113.9 ∠ C1C5H6=127.7 ∠ C1C5F7=118.3
	r(C1F2)=1.389 r(C1H3)=1.103 r(C1H4)=1.103 r(C1C5)=1.439 r(C5H6)=1.113 r(C5F7)=1.334	∠ F2C1H3=108.3 ∠ H3C1H4=107.9 ∠ H4C1F2=108.3 ∠ C5C1F2=110.3 ∠ C5C1H3=111.0 ∠ C5C1H4=111.0	∠ H6C5F7=112.5 ∠ C1C5H6=128.2 ∠ C1C5F7=119.2
	r(C1H2)=1.081 r(C1F3)=1.364 r(C1F4)=1.364 r(C1C5)=1.439 r(C5H6)=1.109 r(C5H7)=1.110	∠ H2C1F3=108.5 ∠ F3C1F4=107.3 ∠ F4C1H2=108.5 ∠ C5C1H2=111.0 ∠ C5C1F3=110.7 ∠ C5C1F4=110.7	∠ H6C5H7=116.1 ∠ C1C5H6=122.1 ∠ C1C5H7=121.8
	r(C1H2)=1.094 r(C1H3)=1.094 r(C1H4)=1.094 r(C1C5)=1.424 r(C5H6)=1.112 r(C5H7)=1.113	∠ H2C1H3=107.7 ∠ H3C1H4=107.7 ∠ H4C1H2=107.7 ∠ C5C1H2=111.2 ∠ C5C1H3=111.2 ∠ C5C1H4=111.2	∠ H6C5H7=113.7 ∠ C1C5H6=123.3 ∠ C1C5H7=123.0

r: Bond lengths in Ångstroms, ∠ : bond angles in degrees.

Now, we are ready to draw the correlation energy diagrams for the addition reactions of hydrogen atoms with ethylene and fluorinated ethylenes, and for the 1,2-migration reactions of fluorine and hydrogen atoms in the radicals produced by the addition reactions. Figures 1,2, and 3 show the results.

TABLE 2

Optimized Geometries for Bridged Structures of Trifluoroethyl, Difluoroethyl, and Ethyl Radicals

Chemical Species	Geometry		
	r(C1F2)=1.337 r(C1F3)=1.338 r(C1F4)=1.504 r(C1C5)=1.400 r(C5H6)=1.115 r(C5H7)=1.116	∠ F2C1F3=106.1 ∠ C5C1F2=127.3 ∠ C5C1F3=126.2 ∠ C5C1F4=62.3 ∠ H6C5H7=113.2 ∠ C1C5H6=120.1	∠ C1C5H7=119.3 ∠ F4C1F2=109.2 ∠ F4C1F3=108.7 ∠ F4C5H6=116.7 ∠ F4C5H7=116.0
	r(C1F2)=1.339 r(C1F3)=1.338 r(C1H4)=1.485 r(C1C5)=1.350 r(C5H6)=1.115 r(C5F7)=1.343	∠ F2C1F3=106.6 ∠ C5C1F2=126.0 ∠ C5C1F3=127.2 ∠ C5C1H4=63.0 ∠ H6C5F7=113.2 ∠ C1C5H6=125.5	∠ C1C5F7=121.2 ∠ H4C1F2=107.2 ∠ H4C1F3=108.3 ∠ H4C5H6=106.1 ∠ H4C5F7=106.0
	r(C1H2)=1.115 r(C1H3)=1.115 r(C1F4)=1.508 r(C1C5)=1.400 r(C5H6)=1.117 r(C5F7)=1.345	∠ H2C1H3=112.0 ∠ C5C1H2=121.7 ∠ C5C1H3=123.1 ∠ C5C1F4=62.3 ∠ H6C5F7=110.6 ∠ C1C5H6=127.3	∠ C1C5F7=121.0 ∠ F4C1H2=113.1 ∠ F4C1H3=113.0 ∠ F4C5H6=112.3 ∠ F4C5F7=107.8
 (cis)	r(C1F2)=1.344 r(C1H3)=1.118 r(C1H4)=1.489 r(C1C5)=1.350 r(C5F6)=1.344 r(C5H7)=1.122	∠ F2C1H3=111.6 ∠ C5C1F2=125.5 ∠ C5C1H3=122.7 ∠ C5C1H4=63.0 ∠ F6C5H7=111.8 ∠ C1C5F6=125.1	∠ C1C5H7=123.0 ∠ H4C1F2=114.6 ∠ H4C1H3=97.2 ∠ H4C5F6=114.5 ∠ H4C5H7=97.4
 (trans)	r(C1F2)=1.342 r(C1H3)=1.118 r(C1H4)=1.494 r(C1C5)=1.350 r(C5H6)=1.117 r(C5F7)=1.341	∠ F2C1H3=111.3 ∠ C5C1F2=122.5 ∠ C5C1H3=126.1 ∠ C5C1H4=63.1 ∠ H6C5F7=111.6 ∠ C1C5H6=126.3	∠ C1C5F7=122.0 ∠ H4C1F2=106.0 ∠ H4C1H3=106.8 ∠ H4C5H6=106.9 ∠ H4C5F7=105.8
	r(C1H2)=1.115 r(C1H3)=1.115 r(C1H4)=1.501 r(C1C5)=1.340 r(C5H6)=1.114 r(C5H7)=1.114	∠ H2C1H3=111.8 ∠ C5C1H2=124.2 ∠ C5C1H3=124.0 ∠ C5C1H4=63.5 ∠ H6C5H7=112.0 ∠ C1C5H6=124.1	∠ C1C5H7=123.8 ∠ H4C1H2=105.4 ∠ H4C1H3=105.3 ∠ H4C5H6=105.3 ∠ H4C5H7=105.2

r: Bond lengths in Ångstroms, ∠ : bond angles in degrees.

From Figs. 1, 2, and 3, it is obvious that the barrier height to the 1,2-migration is higher for hydrogen atom than for fluorine atom in every radical examined. The height for hydrogen atom migration is more than twice that for fluorine

TABLE 3

Total Energies(hartree) Calculated for Open- and Bridged-Trifluoroethyl, Difluoroethyl, and Ethyl Radicals

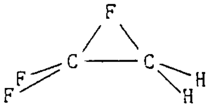
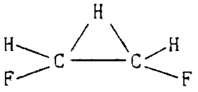
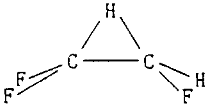
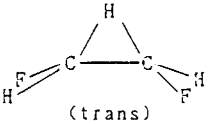
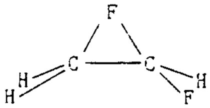
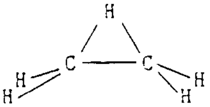
Chemical Species	Total Energy	Chemical Species	Total Energy
CH_2F-CF_2	-94.40640	CH_2F-CHF	-68.70988
CF_3-CH_2	-94.41306	CHF_2-CH_2	-68.71156
CHF_2-CHF	-94.39261	CH_3-CH_2	-17.35814
	-94.37326	 (cis)	-68.63516
	-94.32081	 (trans)	-68.63371
	-68.67254		-17.28759

TABLE 4

Total Energies(hartree) Calculated for Fluorinated Ethylenes, Ethylene, Hydrogen Atom, and Fluorine Atom

Chemical Species	Total Energy	Chemical Species	Total Energy
$CF_2=CHF$	-93.60056	$CHF=CH_2$	-42.24581
$CF_2=CH_2$	-67.93529	$CH_2=CH_2$	-16.56776
cis-CHF=CHF	-67.91402	H	-0.63873*
trans-CHF=CHF	-67.91398	F	-26.25743*

* : Pople's parameters

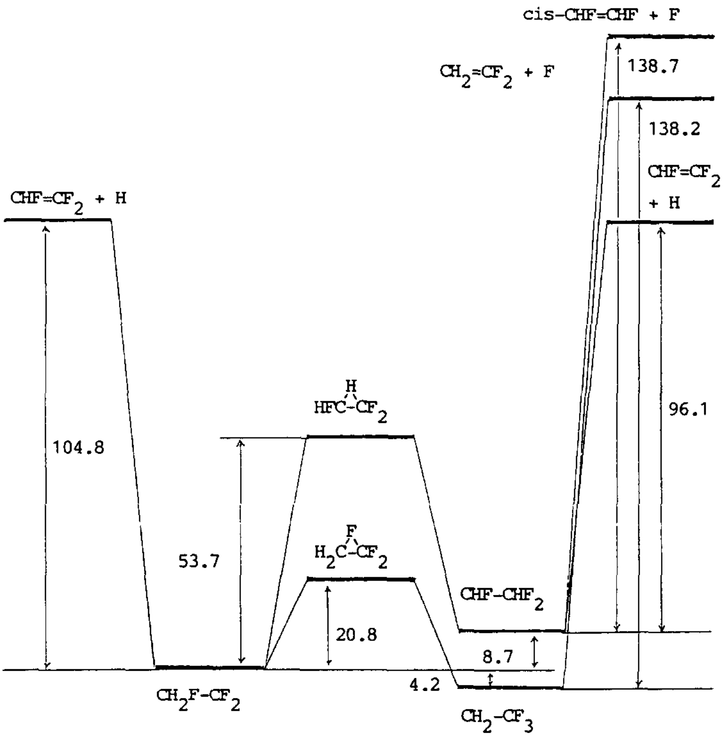


Fig. 1. Energy Profiles (kcal/mol) for 1,2-Migration Processes of Fluorine and Hydrogen Atom in 1,1,2-Trifluoroethyl Radicals

atom. The barrier height to the 1,2-migration of fluorine atom is 2.6 kcal/mol higher in the 1,2-difluoroethyl radical than in the 1,1,2-trifluoroethyl radical, while the barrier height to the 1,2-hydrogen atom migration is higher in the more fluorinated ethyl radical. Therefore, it may be concluded that (1) the 1,2-fluorine atom migration through a fluorine atom bridging intermediate will occur more readily than the 1,2-hydrogen atom migration through a hydrogen atom bridging intermediate in 1,1,2-trifluoroethyl and 1,2-difluoroethyl radical, and (2) a fluorine atom will migrate more readily in the 1,1,2-trifluoroethyl radical than in the 1,2-difluoroethyl radical. On the contrary, (3) a hydrogen atom should migrate more easily in the less fluorinated ethyl radical.

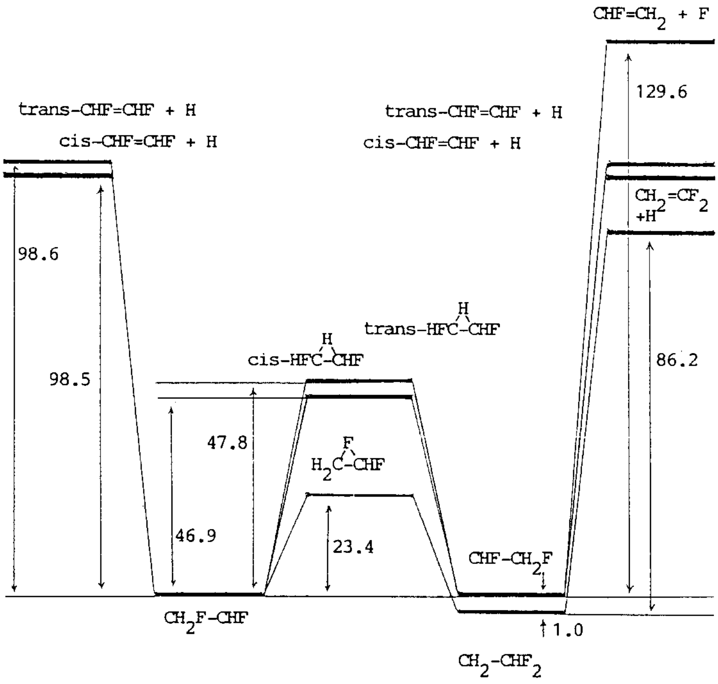


Fig. 2. Energy Profiles (kcal/mol) for 1,2-Migration Processes of Fluorine and Hydrogen Atom in 1,2-Difluoroethyl Radicals

The absolute value obtained by the INDO calculation is not reliable; however, since the standard enthalpies for ethylene and ethyl radical are accurately known, we can normalize all calculated values on this basis, i.e., the barrier height between $CH_2{=}CH_2$ + H and CH_3CH_2 radical which has been estimated to be 95.1 kcal/mol by the INDO should be replaced by 38.9 kcal/mol, which is accurate within 1 kcal/mol[15]. Consequently, the numerical values shown in all Figures should be read by multiplying 0.41(=38.9/95.1), when somewhat quantitative consideration has to be made.

Among the partially fluorinated ethyl radicals, we can recognize that the radical in which fluorine atoms are set aside to one carbon atom is energetically more stable than the radical in which fluorine atoms are distributed over two carbon atoms. In the case of trifluoroethyl radicals, CH_2FCF_2 and

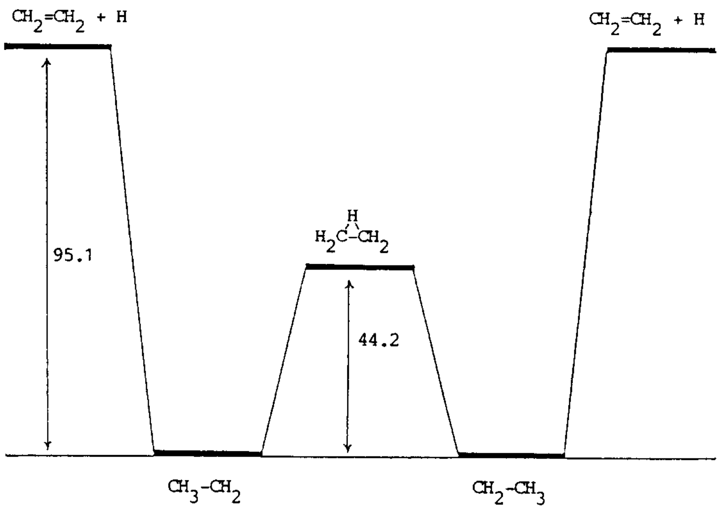


Fig. 3. Energy Profiles (kcal/mol) for 1,2-Migration Process of Hydrogen Atom in Ethyl Radicals

CH_2CF_3, the enthalpy change accompanied by the 1,2-fluorine atom migration can be estimated to be 1.7 kcal/mol(=4.2 x 0.41).

As stated in the Introduction, we have recently studied the 1,2-fluorine atom migration reaction in the trifluoroethyl radical:

$$CH_2FCF_2 \underset{k_b}{\overset{k_f}{\rightleftarrows}} CH_2CF_3$$

and found $k_b/k_f=0.2$. Here, k_f and k_b are the rate constants of the forward and reverse reactions. If the Arrhenius equation can be applied as follows: $k_b=3A\ \exp(-E_b/RT)$ and $k_f= A\ \exp(-E_f/RT)$, then we can estimate $E_b-E_f=1.6$ kcal/mol, which is in good agreement with the enthalpy change estimated above. Similarly, the enthalpy change between difluoroethyl radicals, CH_2FCHF and CH_2CHF_2, can be estimated to be 0.41 kcal/mol(1.0 x 0.41). Consequently, the ratio of rate constants for the forward and reverse reactions can be estimated to be 1.0.

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