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MECHANISM OF *SYN* ADDITION OF MOLECULAR FLUORINE TO ETHYLENE. AN *AB INITIO* MO STUDY*

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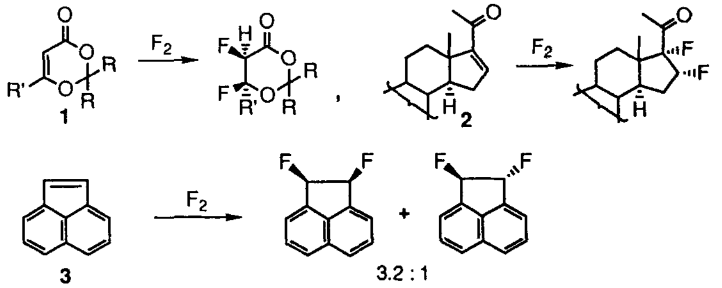
The whole process for the *syn* addition of molecular fluorine to ethylene was analysed at the MP2/6–31 + G level with IRC calculation. The analysis indicates that fluorine approaches the C—C double bond vertically to form a perpendicular complex as the intermediate, which then reorientates to a rhombic-type complex as the transition state to give the final *syn* addition product. This shows that the square-type complex previously proposed is not involved in any stage of the reaction.

INTRODUCTION

The addition of molecular fluorine to ethylenes proceeds stereoselectively to give the *cis* adducts and the method has now gained potential synthetic utility for the preparation of a variety of fluorinated compounds.[1]

Thus, just as in the fluorination of dioxinones (**1**) by molecular fluorine,[2,3] the same reaction using steroidal alkenes (**2**) as the substrates gave solely the *cis* adducts.[4] In contrast, acenaphthylene (**3**),[5] indene[5] and *cis*- and *trans*-propenylbenzenes[6] afforded, in addition to the *cis* addition products, the *trans* adducts in significant amounts (Scheme 1).

To the best of the authors' knowledge, explanations for this preference have only been proposed by Merritt[6,7] and Rozen and Brand[8] in terms of electronic theory. In the proposal made by Merritt, a molecular adduct (**4**; square-type complex) is first formed, which may continue on to products through two competing routes shown in Scheme 2 as paths a and b. A major contribution of the complex **4** via path a will favour direct *cis* addition and will predominate in cases where the incipient carbonium ion **5** is not extensively stabilized. The concomitant formation of the *trans* adducts is due to path b, which is favoured by stabilization of the carbonium ion **5** by a phenyl group (X or Y = Ph). On



Scheme 1

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[*] Cycloaddition in Synthesis, Part 64. For Part 63 see Ref. 9.
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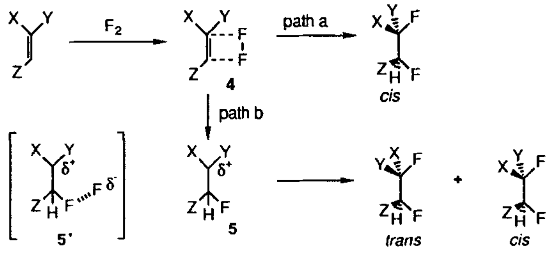


Scheme 2

the other hand, Rozen and Brand proposed another mechanism, in which this addition originates from the initial nucleophilic attack of the double bond on one of the fluorine atoms of molecular fluorine. The resulting tight ion pair (**5**′) collapses before any rotation around the C—C bond in question to give the final *cis* adducts, when there is no leakage to the open carbonium ion **5**.

In the first section of this paper, several complexes, including **4**, accounting for the stereoselectivity are discussed on the basis of HOMO–LUMO theory. In the second section, *ab initio* calculation using ethylene as the substrate is carried out in order to gain further information on the stereoselectivity of the fluorine addition.

QUALITATIVE CONSIDERATION OF THE MECHANISM BASED ON HOMO–LUMO THEORY AND PRINCIPLE OF MAXIMUM OVERLAP

Previously, we have applied Fukui's HOMO–LUMO theory for the addition reaction. Within the assumption that both species should approach in a parallel fashion, we found two types of complex (the square type and rhombic type), as the possible species which determine the observed stereoselectivity.[9] The essence of this paper is summarized in Figure 1. Thus, the square-type complex **4** proposed by Merritt corresponds formally to the two interactions A and B. It should be noted, however, that one cannot exclude the rhombic-type interaction (C), whose overlappings not only partly satisfy the 'criterion of maximum overlap' but also, like A, are all in-phase. The rhombic-type interaction C can be more deformed like D. If one removes the restriction that both components (F_2 and ethylenes) approach in parallel fashion (A–D), the perpendicular interaction E is deduced as a more suitable candidate for attaining $\mathrm{HOMO_{C=C}}$–$\mathrm{LUMO_{F_2}}$ interaction, because E not only is topologically equivalent to D, but also lacks the unfavourable interaction (⤸) existing in D. These interactions (C, D and E) will be mentioned further in the second section. In this section, we shall discuss only about the square-type complex (**4**, interactions A and B).

Previously, Houk[10] reported HOMO and LUMO energies of a variety of ethylenes by surveying the experimental data. Thus, HOMO energies were obtained from a photoelectron spectroscopic study and LUMO energies from polarographic reduction potentials and charge-transfer and electronic spectra. These energies, together with HOMO energy of fluorine obtained by electron impact experiments,[11] are shown in Figure 2. Frontier orbital energies of ethylenes, including 2,2-dimethyl-1,3-dioxin-4-one, and molecular fluorine are presented and coefficients of ethylenes calculated by the AM1 method[12] are given in parentheses.

With these data at hand, two possible square-type MO interactions (A and B) are examined. The energy difference of two MOs for A is *ca* 16–19 eV. The LUMO energy of fluorine has not yet been determined on the basis of the experimental data. The LUMO energy levels obtained by any SCF method are ambiguous in principle, since the SCF procedure accounts only for the occupied orbitals. Nevertheless, taking the AM1 LUMO energy of fluorine as correct, the energy difference for B is *ca* 10–12 eV. At least from energy levels, A is preferred for electron-deficient

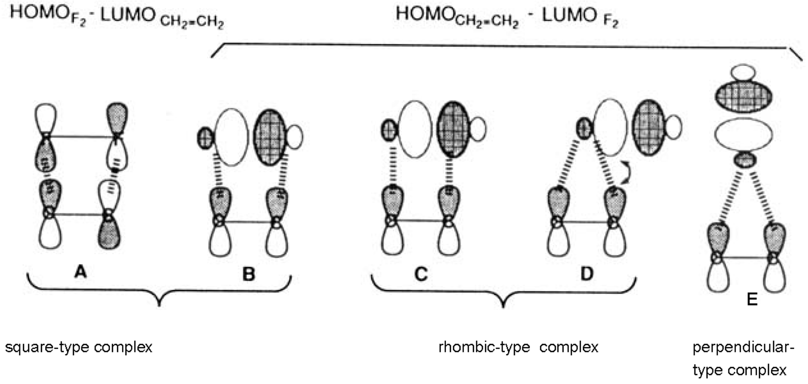


Figure 1. HOMO–LUMO interaction in a variety of complexes

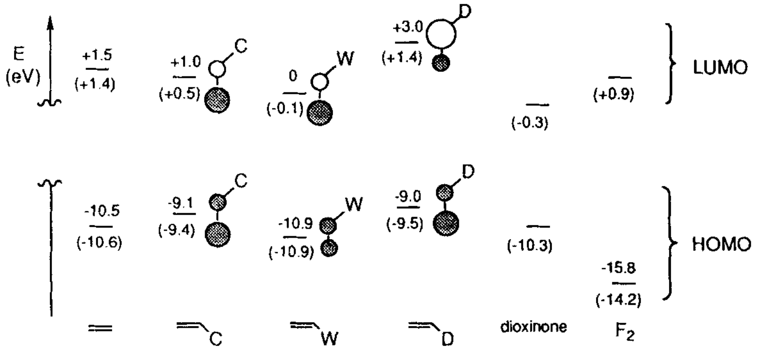


Figure 2. Frontier orbital energies and coefficients estimated on the basis of experimental data and on AM1 calculation (in parentheses). C, CH=CH$_2$; W, CHO; D, OR; dioxinone, 2,2-dimethyl-1,3-dioxin-4-one

ethylenes (C=C—W, W as an electron-withdrawing group) and B for electron-rich and conjugated ethylenes (C=C—D, D as an electron-donating group, and C=C—C, C as a conjugative group). In spite of the larger energy difference of the interaction A, one can prefer A to B from the viewpoint of satisfaction of the 'criterion of maximum overlap.' The reverse interaction (B) for the same square-type complex, on the contrary, violates the above criterion.

The bond distances F—F in the fluorine molecule[13] and C—C in ethylene,[14] both obtained from electron diffraction study, are 1·435 and 1·337 Å, respectively, and therefore interaction A and hence the formation of the complex **4** are also supported on geometrical grounds.

When there is no possibility of **4** being converted into **5**, **4** leads to the *cis* adduct through homolytic F—F bond cleavage [the bond strength of fluorine is only 37 kcal (1 kcal = 4·184 kJ), which is the weakest value in diatomic molecules]. Although this process should not proceed concertedly (${}_{2}\sigma_{s} + {}_{2}\pi_{s}$ cycloaddition is a forbidden reaction), both C—F bonds should be formed on the same side owing to the close proximity of two fluorine radicals.

QUANTITATIVE CONSIDERATION OF THE MECHANISM BY MEANS OF *AB INITIO* CALCULATION

In order to gain further information on the stereoselectivity of the fluorine addition to ethylenes, *ab initio* calculation was carried out using ethylene as the substrate. This section describes the results in detail.

First, an *ab initio* 6–31 + G level calculation[15] was carried out for the square-type complex **4** in order to obtain quantitative information on its structural properties. When the intermolecular distance was fixed at 1·8 Å (note that C—C and F—F bonds are in parallel with each other for both square- and rhombic-type complexes), the net positive charge of a fluorine atom increased by 0·153 owing to the electron shift from fluorine to ethylene. This supports the view that, in such a complex, the interaction due to HOMO$_{F_2}$ and LUMO$_{C=C}$ (A) actually plays the major role.

To confirm the reverse electron flow in the rhombic-type complex **6** as suggested by the HOMO–LUMO theory, the following calculation was carried out. By keeping the vertical distance (d) again at 1·8 Å, the variation of total net charges of fluorine with the horizontal distance (l) between the centres of gravity of F—F and C—C bonds is determined and the results are depicted in Figure 3.

Figure 3 indicates that in the rhombic-type complex **6**, the electron shift from ethylene to fluorine increases as predicted by the aforementioned HOMO–LUMO theory with increasing horizontal distance (l). It should be noted, however, that the energy of the complex increases (in other words, the complex is destabilized) with decreasing horizontal distance (rhombic-type → square-type). This means that, if one assumes that the vertical distance is 1·8 Å, the square-type complex is less adequate than the rhombic-type one on energetic grounds.

Next, we examined the possible transition state and the reaction path of the addition reaction. When *ab initio* calculation was carried out at the Hartree–Fock level with the 6–31 + G basis set, the perpendicular complex **7** was deduced to be a suitable transition state.

Although the geometrical structures of many molecules can be deduced within the Hartree–Fock framework, it is well known that the method is hardly applicable to structures of the transition state. The calculation using the MP2 (second-order Møller–Plesset) method[16] may reproduce structural data of the transition state more accurately than the Hartree–Fock computations.[17] Therefore, the above reaction was examined by the MP2 method with the same basis set

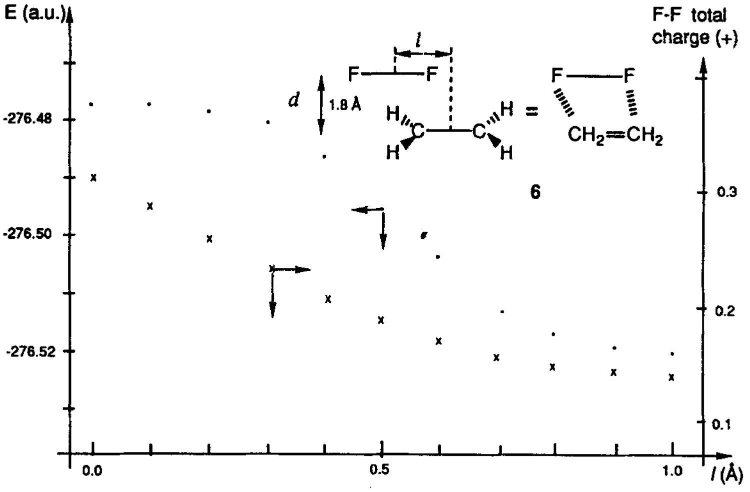


Figure 3. Variation of (•) the potential energies and (×) the net fluorine charges of the interacting species with the horizontal distance (l)

(6–31 + G). As a result, the deformed rhombic-type complex **8** was deduced as the transition state.

In order to elucidate the whole process, the reaction path was traced from the transition state **8** to the reactants (ethylene and molecular fluorine) and to the product (1,2-difluoroethane) by use of the IRC (intrinsic reaction coordinate) algorithm developed by Gonzalez and Schlegel.[18] The result obtained is shown in Figure 4, with essential parameters in Table 1. When the distance between fluorine and ethylene is approximately 4 Å, the total energy begins to decrease. Then the perpendicular complex **7** is formed as the intermediate. With progress of the reaction, fluorine approaches the C—C double sideways bond to give the product through the transition state **8**. As the reaction proceeds, the C—C and F—F bond lengths become longer and the net negative charge of fluorine increases owing to the electron shift from ethylene to fluorine. At

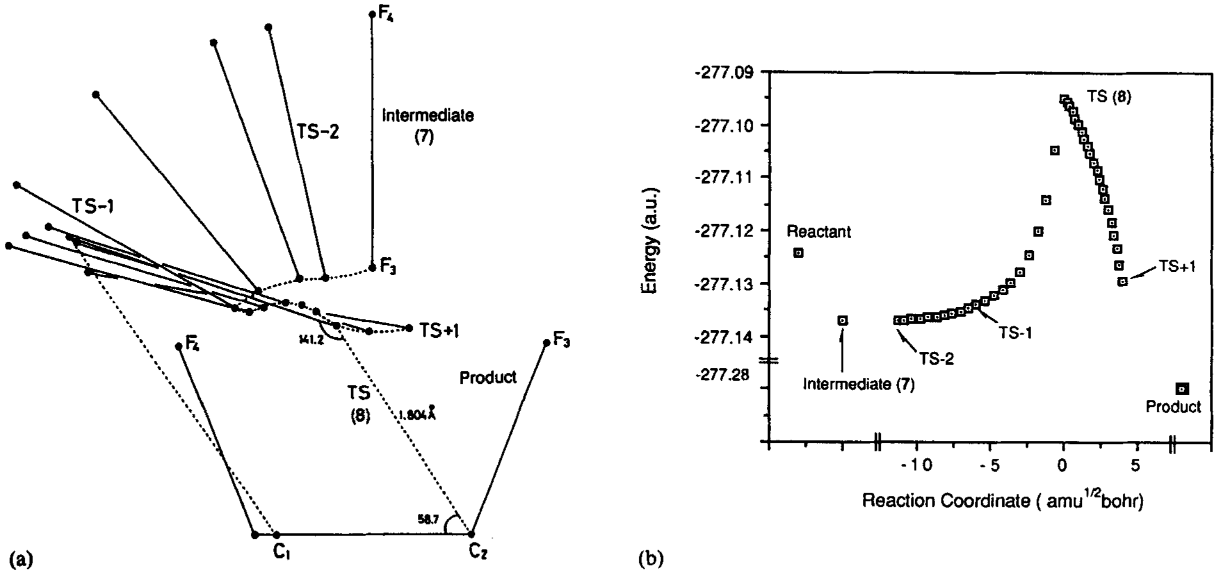
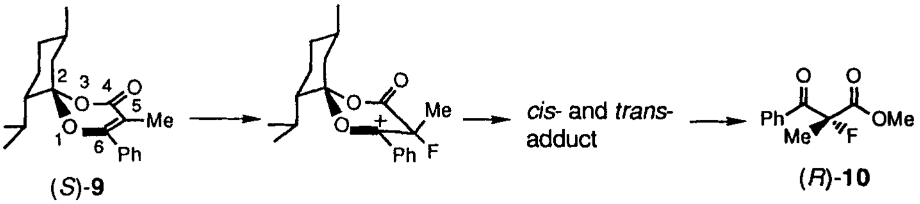


Figure 4. Optimized geometries and potential energy profiles (in a.u.) for the addition of molecular fluorine to ethylene at the MP2/6–31 + G level. Only essential parameters are shown in Table 1

Table 1. Essential data for the results shown in Figure 4

Species	E (a.u.)	C_1—C_2 (Å)	F_3—F_4 (Å)	C_2—F_3 (Å)	F_3 charge	F_4 charge
Reactant	−277·12426	1·355	1·515	∞	0	0
Intermediate	−277·13704	1·393	1·793	2·059	+0·06	−0·35
TS-2	−277·13693	1·396	1·801	2·172	+0·06	−0·36
TS-1	−277·13320	1·431	1·829	2·351	+0·02	−0·48
TS	−277·09474	1·463	2·028	1·804	−0·02	−0·88
TS+1	−277·12924	1·502	2·363	1·563	−0·15	−0·77
Product	−277·27903	1·551	2·615	1·468	−0·33	−0·33



Scheme 3

the transition state **8**, the net negative charge of F_4 takes the largest value of −0·88.

In order to support the above view, it is interesting to mention the high diastereofacial selectivity observed in the addition of fluorine to chiral spirocyclic dioxinones. Like the Diels–Alder, photo[2 + 2]cycloaddition and related pericyclic reactions, the addition takes place from the isopropyl side.[19] Since the transition states of the above pericyclic reactions are expected to be similar (at least in a stereochemical sense) to **8**, the diastereofacial selectivity observed on addition of fluorine to dioxinones is also expected to take place from the less hindered isopropyl side. Thus, whereas the fluorination of the chiral spirocyclic 5-methyl-6-phenyl-1,3-dioxin-4-one [(*S*)-**9**] (Scheme 3) afforded the *cis*- and *trans*-difluorides, the enantiomeric excess of the β-keto ester [(*R*)-**10**] obtained by the cleavage of the acetal function was almost 100%.[20] This observation clearly shows that the formation of a C_5—F bond is the first step in the addition reaction.

In the case of the rhombic-type complex ($\text{HOMO}_{\text{dioxinone}}$–$\text{LUMO}_{F_2}$ = interaction D) derived from 2,2-dimethyl-1,3-dioxin-4-one, the formation of a C_5—F bond may take place prior to that of a C_6—F bond because of the larger HOMO coefficient at the 5-position than that of the 6-position (AM1 calculation, Figure 5). If the reverse interaction takes the major role as suggested by the interaction (A: HOMO_{F_2}–$\text{LUMO}_{\text{dioxinone}}$), the larger LUMO coefficient at the 6-position than that of the 5-position indicates C_6—F bond formation as the first step. Since such a deduction does not agree with the experimental result (see above), it can be concluded that in the fluorine addition to the dioxinone (*S*)-**9** the reverse interaction (A) does not play a significant role.

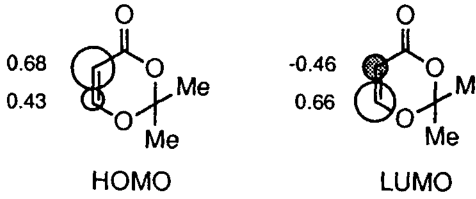


Figure 5. HOMO and LUMO coefficients of 2,2-dimethyl-1,3-dioxin-4-one obtained by AM1 calculation

CONCLUSION

The results shown in Figure 4 indicate the following path. First, a vertical approach of fluorine to the middle of the C—C bond of ethylene gives rise to the perpendicular-type complex **7** as the intermediate. Then, within such a complex, fluorine shifts sideways to the C—C double bond to give the transition state **8**. The complex **7** corresponds to interaction E and the latter to interaction D. Therefore, it can be concluded that addition of fluorine to ethylene and the dioxinones should be categorized as an electrophilic reaction, and does not proceed via the square-type complex **4** as the transition state. The clarification of the mechanism concerning the addition reaction using electron-deficient alkenes (e.g. acrylonitrile and alkyl acrylate) as the substrate remains a problem to be solved.

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