Ab-initio Mechanistic Studies of Radical Reactions. Directive Effects in the Addition of Methyl Radical to Unsymmetrical Fluoroethenes

Roger Arnaud and Robert Subra
Université Scientifique et Medicale-LEDSS VII, B.P. 68 38042 St. Martin d'Heres Cedex, France
Vincenzo Barone* and Francesco Lelj
Dipartimento di Chimica, Università di Napoli, via Mezzocannone, 4-80134 Napoli, Italy
Santiago Olivella and Albert Solé
Facultat de Quimica, Universitat de Barcelona, Av. Diagonal, 647-08028 Barcelona, Spain
Nino Russo
Dipartimento di Chimica, Università della Calabria 87030 Arcavacata di Rende (CS), Italy

Addition of methyl radical to unsymmetrical fluoroethenes has been studied by *ab-initio* molecular orbital calculations. In agreement with experimental data, we find that the reaction rate decreases in going from ethene to mono- and 1,1 di-fluoroethene, but sharply increases in the case of trifluoroethene. Additions to the more fluorinated carbon atoms are always thermodynamically favoured, but addition to the CH_2 end of mono- and 1,1 di-fluoroethene is kinetically favoured. The general trends of the potential energy barriers have been rationalized by means of the energy decomposition scheme proposed by Morokuma. Non potential energy effects have also been considered, but their role is negligible.

Alkyl radical additions to substituted alkenes have received a great deal of attention from an experimental point of view since they are among the most important processes in a variety of free-radical chain reactions.[1–3] Although some empirical rules have been proposed to rationalize the origin of directive effects and of selectivity in such reactions, it has been concluded that 'no simple property could be used to determine the orientation of free radical additions' which results from 'the complex interplay of polar, steric, and bond strengths terms'.[2] Fluorinated ethenes are among the most studied substrates in this connection and the addition of an H atom[4] or alkyl radicals[1a,5] usually results in preferential attack at the less substituted carbon atom. However, the methyl radical shows anomalous behaviour[6] since its attack occurs preferentially at the CH_2 end of fluoroethene and 1,1-difluoroethene, but at the CF_2 end of trifluoroethene. The origin of this reversal in regioselectivity has been the subject of several discussions,[1,7] but no entirely satisfactory explanation has been given to date. The existence of a linear relationship between relative reaction rates of different fluoroethenes and corresponding (experimental) activation energies suggests the absence of complicating entropy effects with the possible exception of methyl addition to the CF_2 end of trifluoroethene. Different entropy effects have indeed been suggested as one of the reasons for the unexpected inversion in orientation ratios for the addition of trifluoromethyl and methyl radicals to trifluoroethene[8] since semiempirical quantum mechanical methods predict a lower activation enthalpy for the addition both of CH_3 and CF_3 to the CHF end of trifluoroethene.[8–10] While semiempirical computations have been able to give good numerical results, we think that an analysis of the different effects playing a role in determining reactivity variations requires *ab-initio* computations which do not involve adjustable (and hence scarcely controllable) parameters. Several *ab-initio* studies are available for the addition of H atoms to ethenic substrates,[11–21] but only a few of them[20,21] explicitly deal with directive effects. The situation is even worse in the case of methyl addition since, to the best of our knowledge, only ethyne and ethene have been considered so far.[22–24] This situation prompted us to perform a systematic study of methyl radical addition to unsymmetrical fluoroethenes by the non-empirical Hartree–Fock method employing a split-valence basis set, which provides a quite effective compromise between the reliability of results and the computer time.[17,21,23] Vibrational frequencies have also been computed in order to analyse the relative weight of enthalpic and entropic factors in determining the rate constants. The main concern of the study is not the numerical accuracy of the thermodynamic results, but, rather, the correct reproduction of general trends and their interpretation in terms of chemically interpretable contributions. To this end we have applied the decomposition technique proposed by Morokuma[25] and discussed the results with special reference to the analogous additions of hydrogen atoms.

Notation and Method.—*Ab-initio* calculations were performed with the GAUSSIAN/80 system of programs[26] using the restricted Hartree–Fock (RHF) method for closed-shell systems and the unrestricted Hartree–Fock (UHF) method for open-shell systems. We have used the 4-31G basis set[27] for geometry optimizations (performed by the Schlegel algorithm[28] employing analytical gradients) and evaluation of Cartesian force constants by numerical differentiation of the gradient. Normal modes and vibrational frequencies were then obtained by diagonalization of the matrix of mass-weighted Cartesian force constants.

The zero-point vibrational energies (ZPE), absolute entropies (S°), and specific heats (c°) were computed by standard methods[29] from the frequencies calculated at the 4-31G level and multiplied by a scaling factor (0.89) to correct the electron correlation and the vibrational anharmonicity effects.[23,30,31] The rate constants $k(T)$ are then computed using the activated complex theory: (1)[32,33] where χ is the transmission coefficient

$$k(T) = \chi\frac{KT}{h}K_c^{\ddagger} = \chi\frac{KT}{h}(R'T)^{-\Delta n^{\ddagger}}K_p^{\ddagger} =$$
$$\chi\frac{KT}{h}(R'T)^{-\Delta n^{\ddagger}}\exp\frac{(\Delta S^{\ddagger})}{R}\exp\frac{(-\Delta H^{\ddagger})}{RT} = A\exp\frac{(-E_a)}{RT} \quad (1)$$

(usually taken equal to 1); $K_p^{\ddagger}$ and $K_c^{\ddagger}$ are pseudo-equilibrium constants (involving the transition structure and the reactants) in units of pressures and concentrations, respectively; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy changes between reactants and transition structures; $\Delta n^{\ddagger}$ is the variation in the number

Table 1. Comparison between harmonic frequencies (in cm^{-1}) and thermodynamic functions (in dimensionless units) computed at the 4-31G level and (in brackets) experimental values (C_2H_4 from ref. 41; C_2H_3F from ref. 42; $C_2H_2F_2$ from ref. 43; C_2HF_3 from ref. 44; and CH_3 from ref. 45) for ethylene, fluoroethenes, and methyl radical

Approx. Assign	C_2H_4	C_2H_3F	$C_2H_2F_2$	C_2HF_3	CH_3
str. CH	b_{2u} 3 408 (3 106)	a′ 3 467 (3 150)	b_1 3 489 (3 171)	a′ 3 499 (3 150)	3 444 (3 150)
str. CH/CF	b_{1g} 3 377 (3 103)	a′ 3 443 (3 115)	a_1 3 389 (3 101)	a′ 1 503 (1 362)	3 444 (3 150)
str. CH/CF	a_g 3 300 (3 026)	a′ 3 356 (3 080)	b_1 1 444 (1 280)	a′ 1 377 (1 264)	3 260 (3 044)
str. CH/CF	b_{3u} 3 304 (3 021)	a′ 1 257 (1 156)	a_1 974 (915)	a′ 988 (929)	
str. CC	a_g 1 856 (1 630)	a′ 1 889 (1 654)	a_1 1 967 (1 728)	a′ 2 036 (1 788)	
scis.	b_{3u} 1 639 (1 444)	a′ 1 580 (1 380)	a_1 1 588 (1 359)	a′ 1 234 (1 171)	1 545 (1 385)
scis.	a_g 1 521 (1 342)	a′ 1 462 (1 306)	a_1 550 (549)	a′ 498 (485)	1 545 (1 385)
rocking	b_{1g} 1 386 (1 220)	a′ 1 010 (929)	b_1 1 091 (949)	a′ 650 (623)	
rocking	b_{2u} 935 (826)	a′ 520 (483)	b_1 473 (439)	a′ 248 (232)	
wagging	b_{1u} 1 125 (949)	a″ 1 121 (940)	b_2 1 091 (810)	a″ 983 (750)	469 (612)
wagging	b_{2u} 1 162 (943)	a″ 1 098 (863)	b_2 659 (603)	a″ 630 (555)	
twist	a_u 1 168 (1 073)	a″ 791 (711)	a_2 812 (714)	a″ 335 (305)	
mean ($\nu_{exp}/\nu_{4\text{-}31G}$)	0.89	0.89	0.91	0.91	0.98
$S°/R^a$	26.27 (26.37)	30.40 (30.39)	32.01 (31.93)	35.33 (35.28)	23.53 (23.65)
$c_p°/R^a$	5.05 (5.14)	6.01 (6.06)	7.13 (7.13)	8.40 (8.35)	4.84 (4.28)
ZPE/RT^a	15.50 (15.60)	13.44 (13.50)	11.22 (11.24)	8.95 (9.07)	8.78 (9.16)

[a] At 298 K.

of particles in going to the transition structure (−1 for a bimolecular reaction); K is the Boltzmann constant, R the ideal gas constant (in units coherent with those employed for the enthalpy and entropy), R' has the same meaning, but in litre inverse atmospheres (0.082), T is the absolute temperature, and h is the Planck constant. From equation (1) we get

$$A = \chi\frac{KT}{h}(R'T)^{-\Delta n^{\ddagger}}\exp(1 - \Delta n^{\ddagger})\exp\frac{\Delta S^{\ddagger}}{R} = \chi\frac{KT}{h}\exp\left(1 - \Delta n^{\ddagger} + \frac{\Delta S_c^{\ddagger}}{R}\right)$$

$$E_a = \Delta H^{\ddagger} + (1 - \Delta n^{\ddagger})RT = \Delta U^{\ddagger} + RT = \Delta E^{\ddagger} + \Delta(ZPE) + RT + \Delta T'$$

with

$$\Delta S_c^{\ddagger} = \Delta S^{\ddagger} - R\Delta n^{\ddagger}\ln(R'T)$$

$$\Delta T' = \int_0^T \Delta c_v^{\ddagger}\mathrm{d}T = 3\Delta n^{\ddagger}RT + \Delta\{\Sigma h\nu_j/[\exp(h\nu_j/KT) - 1]\}$$

In the above equations $\Delta U^{\ddagger}$ and $\Delta E^{\ddagger}$ are respectively the internal and potential energy changes between reactants and transition structures. The term $\Delta T'$ is usually very small (*vide infra*) and has been neglected in our previous studies.[23,34]

For deeper understanding and for the chemical interpretation of the addition mechanism, the reaction barrier $\Delta E^{\ddagger}$ is expressed as a sum of the intramolecular deformation ($E_{def.}$) energy and of the intermolecular interaction energy ($E_{int.}$), which, in turn, consists of electrostatic (E_{es}), exchange repulsion (E_{ex}), polarization (E_{pl}), charge transfer (E_{ct}), and mixing (E_{mix}) energies.[25]

In order to distinguish the different structures in the discussion we use the following nomenclature: each olefin is denoted by its number of fluorine atoms (F1 for fluoroethene, F2 for 1,1-difluoroethene, and F3 for trifluoroethene) and its carbon atoms are labelled 1 (the less fluorinated one) and 2 (the more fluorinated one). Then the other structures are denoted by a letter distinguishing transition states (TS) from products (P) followed by the number of the carbon atom attacked by CH_3 and the label of the parent olefin, Ethylene, propyl radical, and the transition state are denoted by E, PE, and TSE, respectively.

Results and Discussion

1. *Fluoroethenes: Geometries and Vibrational Frequencies.*—The 4-31G-optimized geometries of fluoroethenes are given in Figure 1. The optimized geometries of fluoroethene and 1,1-difluoroethene have been previously reported,[14,35] but in the former case we have obtained a slightly different geometry of lower energy. The sensitivity of bonds involving fluorine to basis set and correlation effects has been studied in some detail.[36,37] Split-valence basis sets such as 4-31G overestimate the CF bond lengths, while the addition of polarization functions results in underestimation. Electron correlation in general increases bond lengths. Comparison with the experimental geometries of fluoroethenes[38–40] confirms this effect, but shows that the 4-31G basis set is able to reproduce the reduction both of CF and C=C bond lengths with the increase in fluorination.

Table 1 summarizes the vibrational frequencies of fluoroethenes, which, on average, are *ca.* 11% higher than the experimental values, as usually found with split-valence basis sets.[17,23,30] Although more refined procedures (*e.g.* the use of different scale factors for different types of vibrations) are preferable in the assignment of vibrational spectra, the simpler uniform scaling by 0.89 which we use in the present work provides very good zero-point energies (ZPE) and vibrational entropies (see Table 1).

The most apparent trends in the frequencies of fluoroethenes concern the C=C bond; in fact the frequency associated with C=C stretching increases upon fluorination, whereas that associated with torsion decreases. This suggests that the σ bond strength increases upon fluorination, whereas the π bond strength decreases at the same time. This interpretation is in agreement with the larger reduction of the C=C bond length upon fluorination in the product radicals than in the fluoroethenes since in the former case the π contribution is far less important. Our computations for 1,1-difluoroethene allow us to solve the controversy over the two values reported for the torsional frequency (714 cm^{-1} according to ref. 43 and 590 cm^{-1} according to ref. 46) in favour of the higher value. Much lower frequencies are obtained for the out-of-plane bendings when fluorine atoms are involved, and this is in agreement with the increase of pyramidality which accompanies fluorine substitution in alkyl radicals.

2. *Product Radicals: Geometries and Reaction Energies.*—The potential energy surfaces of these compounds show several minima of similar energy; we give in Figure 1 and Table 2 only the optimized structure of the most stable conformation

Table 2. Dihedral angles for transition states and products in the additions of CH$_3$ to fluoroethenes. The deviations from planarity at the different centres δ_i (see text for definition) are also given

CH$_3$ Attacks on C-1

	CH$_3$–CH$_2$CHF		CH$_3$–CH$_2$CF$_2$		CH$_3$–CHFCF$_2$	
Parameter	TS	Product	TS	Product	TS	Product
4,1,2,6	18.9	58.1	25.0	57.6	29.4	52.0
5,1,2,7	18.5	43.6	25.0	57.6	28.6	64.3
δ_1	5.6	35.7	5.5	36.5	6.6	37.6
6,2,1,3	83.6	63.5	78.3	64.3	74.5	73.1
7,2,1,3	86.2	78.6	78.3	64.3	77.5	55.7
δ_2	0.7	10.2	3.6	20.3	5.4	21.2
8,3,1,2	175.9	178.5	180.0	180.0	179.8	178.0
9,3,1,2	56.2	58.6	60.1	60.2	61.1	62.1
10,3,1,2	63.9	61.4	60.1	60.2	59.5	58.4
δ_3	11.0	35.3	9.5	34.9	7.0	33.3

CH$_3$ Attacks on C-2

	CH$_3$–CHFCH$_2$		CH$_3$–CF$_2$CH$_2$		CH$_3$–CF$_2$CHF	
Parameter	TS	Product	TS	Product	TS	Product
4,1,2,3	91.6	176.9	85.7	180.0	85.1	180.0
5,1,2,3	81.9	5.3	85.7	0.0	79.5	0.2
δ_2	6.9	36.4	8.7	37.7	9.0	39.1
4,1,2,6	15.0	60.7	22.1	56.7	23.5	56.4
5,1,2,7	23.1	132.0	22.1	123.7	27.5	123.2
δ_1	0.3	0.5	0.6	0.0	1.7	0.0
8,3,2,1	179.0	177.0	180.0	180.0	178.1	179.5
9,3,2,1	60.4	57.3	61.0	60.3	62.4	60.8
10,3,2,1	60.6	62.8	61.0	60.3	59.1	59.6
δ_3	10.7	34.1	8.5	32.6	6.9	32.3

obtained at the 4-31G level. Some regular trends deserve mention.

(i) For each substrate the radical resulting from the addition at the less substituted carbon atom prefers a *gauche* conformation, whereas addition at the more fluorinated centre always results in a staggered or quasi-staggered conformation. Comparison of radicals which have identical β-substituents but different α-ones (*e.g.* P2F1 and P1F3) or *vice versa* (*e.g.* P1F1 and P2F3) suggests that β-fluorine substituents induce a preference for staggered over *gauche* conformers, the opposite being true for α-fluorine substituents. (ii) For all the radicals the C(3)–C bond is shorter when the methyl group is borne by the more substituted carbon atom.

A crude measure of deviation from planarity at the carbon C-1 can be given by $\delta_i = 360°$ minus the sum of the three valence angles around the examined centre (the larger the value of δ_i, the more the site is pyramidalized). Inspection of the values reported in Table 2 shows that: (iii) the pyramidalization of the carbon atom undergoing attack increases with the number of fluorine atoms borne by the centre and also with the total number of fluorine atoms in the radical. (iv) The radical centre is also pyramidalized, as expected, in the *gauche* conformation and the deviation from planarity increases with the number of fluorine substituents on the site; on the other hand, the radical site remains planar or nearly planar in the staggered conformations. (v) The pyramidality of the methyl group is slightly larger when it is bonded to the less substituted end of a given substrate. This trend parallels the deformation energy of the methyl group at the corresponding transition states (see next section).

All the addition reactions are strongly exothermic and the computed value of ΔE_R for the prototype reaction between methyl radical and ethylene (95 kJ mol^{-1}) is in good agreement value of 94 kJ mol^{-1} obtained from the experimental enthalpies of formation: CH$_3$ = 142.2 kJ mol^{-1},[47] C$_2$H$_4$ = 52.3 kJ mol^{-1},[48] and propyl radical = 100.5 kJ mol^{-1}.[49]

It is worth noting that the computed exothermicity of the addition reactions increases with the total number of fluorine atoms and, for a given olefin, the more exothermic reaction always corresponds to the addition at the more fluorinated carbon atom, the largest difference between the two edges being obtained for the most chemically unsymmetrical olefin, *i.e.* 1,1-difluoroethene. This trend indicates that the stabilizing effect of fluorine atoms is (i) more effective in fluoropropyl radicals than in the corresponding fluoroethenes; and (ii) operative both at α- and β-positions. As far as the β-effect is concerned, it is well known that C–C bonds are stabilized by unsymmetrical substitution with electronegative atoms since the electronegativity difference between the two fragments increases the role of stabilizing interfragment charge-transfer interactions.[50] It is noticeable that, on these grounds, the effect of β-fluorine atoms will depend on the nature of the attacking radical and will tend to be reversed along the series CH$_3$, CH$_2$F, CHF$_2$, CF$_3$ with profound effects also on the reactivity (see section 3).

3. *Transition States: Geometries and Arrhenius Parameters.*— The energies and geometries of all the transition structures (Figure 1 and Table 2) more closely resemble the olefins than the product radicals, as expected for very exothermic reactions. In fact, the length R of the carbon–carbon bond being formed (see Figure 2) is long (> 2.2 Å) and the C(1)–C(2) bond lengths of the substrates (r) are much nearer to reactant than to product ones. It should be noted that, at variance with the results previously obtained for the attack of hydrogen,[20] the angle between the methyl group and the olefin (α) is practically constant (about 108°) in all the transition structures except TS1F3.

In each case the carbon being attacked pyramidalizes away from the approaching radical, whereas the other carbon pyramidalizes toward the incoming radical. Comparison with previous computations suggests that the transition structures for methyl attack are more advanced on the reaction path than for H addition since the ratio of the distances corresponding to the new C–C bond in the transition states and corresponding products are lower in the former case (for example the ratios for TS1F2 and TS2F2 are 1.49 and 1.52 for CH$_3$, to be compared with 1.81 and 1.78 for H[20]). For a given substrate the R distance is longer when CH$_3$ attacks the less substituted carbon atom and this trend is the same as for the product radicals. However, if we consider the difference ΔR between this bond length at the TSs and in the products it is quite apparent that earlier transition states are obtained upon attack of methyl at the more substituted carbon atom of a given substrate (ΔR is 0.696 *versus* 0.707 Å for fluoroethene; 0.753 *versus* 0.774 Å for 1,1-difluoroethene; and 0.841 *versus* 0.850 Å for trifluoroethene). Moreover, ΔR increases with the total number of fluorine atoms in the olefin.

The progress of the other geometrical parametres (x) at the transition state can be defined as $\Delta x = (x_{TS} - x_{react.})/(x_{prod.} - x_{react.})$. The corresponding value Δr for the C(1)–C(2) bond length is about 0.35 for all the systems studied, but is slightly larger for attack at the more substituted carbon atom of a given olefin and generally increases with the total number of fluorine atoms in the olefin. The relative pyramidalization of the attacked carbon atom ($x = \delta_i$) varies between 0.15 and 0.23 and is always greater when the methyl radical attacks the C-2 atom of the different olefins. An opposite trend is found for the structural modifications of the methyl fragment ($x = \delta_3$): in fact its relative pyramidalization decreases with the increase in the total number of fluorine atoms, but is only negligibly affected by the degree of substitution at the attacked carbon atom (TS1F1:0.31, TS2F1:0.31, TS1F2:0.27, TS2F2:0.26, TS1F3:0.21, TS2F3:0.21).

We can therefore conclude that the different geometrical parameters do not agree with a definite ordering from earlier to later transition states. Anyway, the ordering based on ΔR seems the most convincing in view of the fact that R is (i) the geometrical parameter which undergoes the largest modification between reactants and products, and (ii) by far the largest component of the transition vectors (*vide infra*).

The 4-31G vibrational frequencies of all the transition structures are reported in Table 3. The methyl radical and fluoroethene molecules have 6 and 12 vibrational degrees of freedom, respectively. There are 24 in the transition states, one of which corresponds to the reaction co-ordinate. There is therefore a net gain of five vibrational degrees of freedom with respect to the gain of only two degrees of freedom which occurs in atom additions. This explains why the zero-point correction to the activation energy is more important in methyl than in hydrogen additions to alkenes.[23] In all the transition structures the normal co-ordinate for the imaginary frequency (*i.e.* the transition vector) is predominantly the radical-substrate C–C stretch, with a small contribution of the out-of-plane bending at the attacked carbon atom. Larger frequencies always correspond to methyl attack at the more substituted end of each olefin, but the frequency does not always increase with the total number of fluorine atoms. Since we are in the presence of early transition states, the imaginary frequencies could be directly related to energy barriers: this correlation works remarkably well (very similar $\Delta E^{\ddagger}$ and imaginary frequencies are obtained for TSE, TS1F1, and TS1F2, which are lower than the very similar values obtained for TS2F1 and TS2F2; the values of TS1F3 are lower than the previous ones) with the only exception of TS2F3 whose imaginary frequency, contrary to the corresponding $\Delta E^{\ddagger}$, is higher than that of TS1F3. The difference between TS1F3 and TS2F3 is in any case much lower than the difference between TS1F1 and TS2F1 or TS1F2 and TS2F2. The new vibrational modes arising from the lost rotational and translational degrees of freedom of methyl and olefin have very low frequencies and, in the case of methyl addition to ethylene, are well separated from the original normal mode of CH_3 and

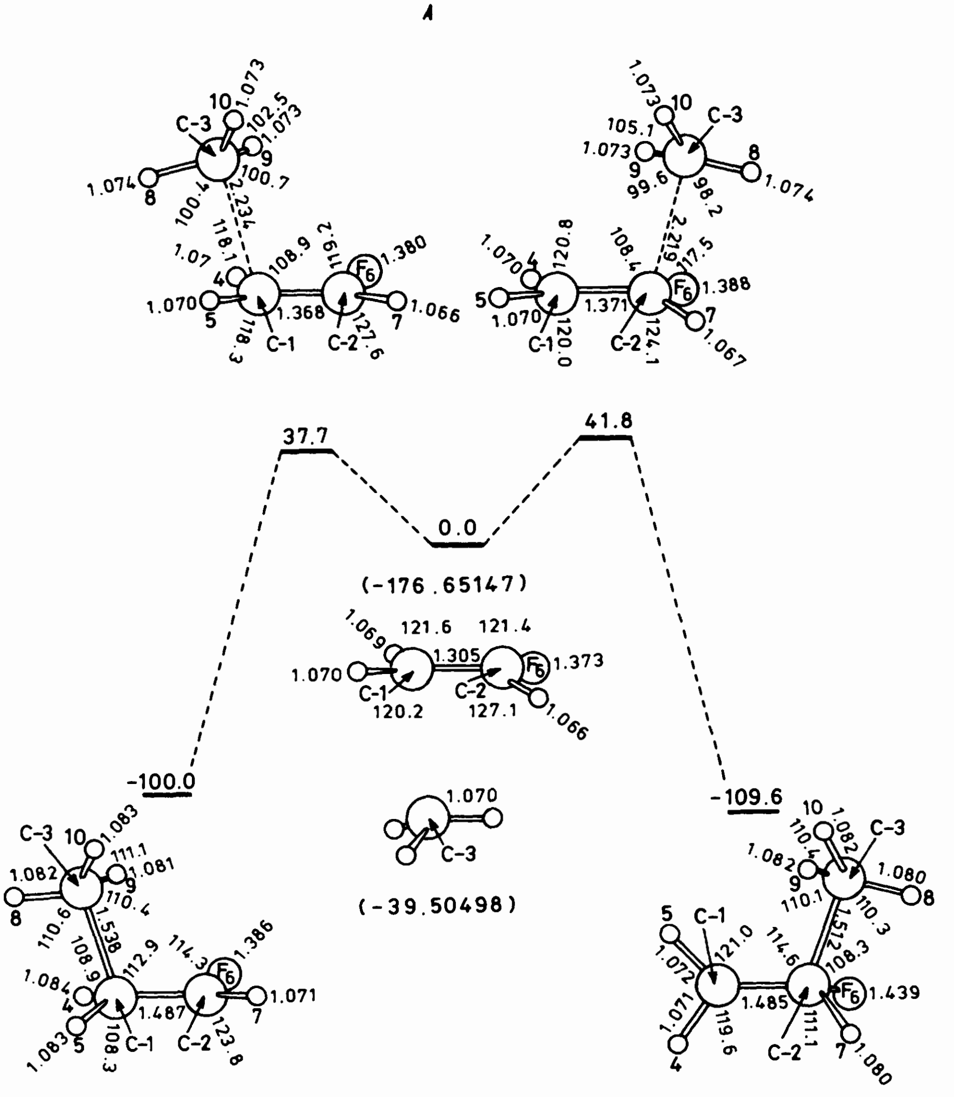

Figure 1. Bond lengths (in Å), valence angles (in degrees), potential energy barriers, and reaction energies (in kJ mol^{-1}) obtained at the 4-31G level for the addition of methyl radical to fluoroethene (*A*), 1,1-difluoroethene (*B*), and trifluoroethene (*C*). The total energies of reactants (in a.u.) are given in brackets

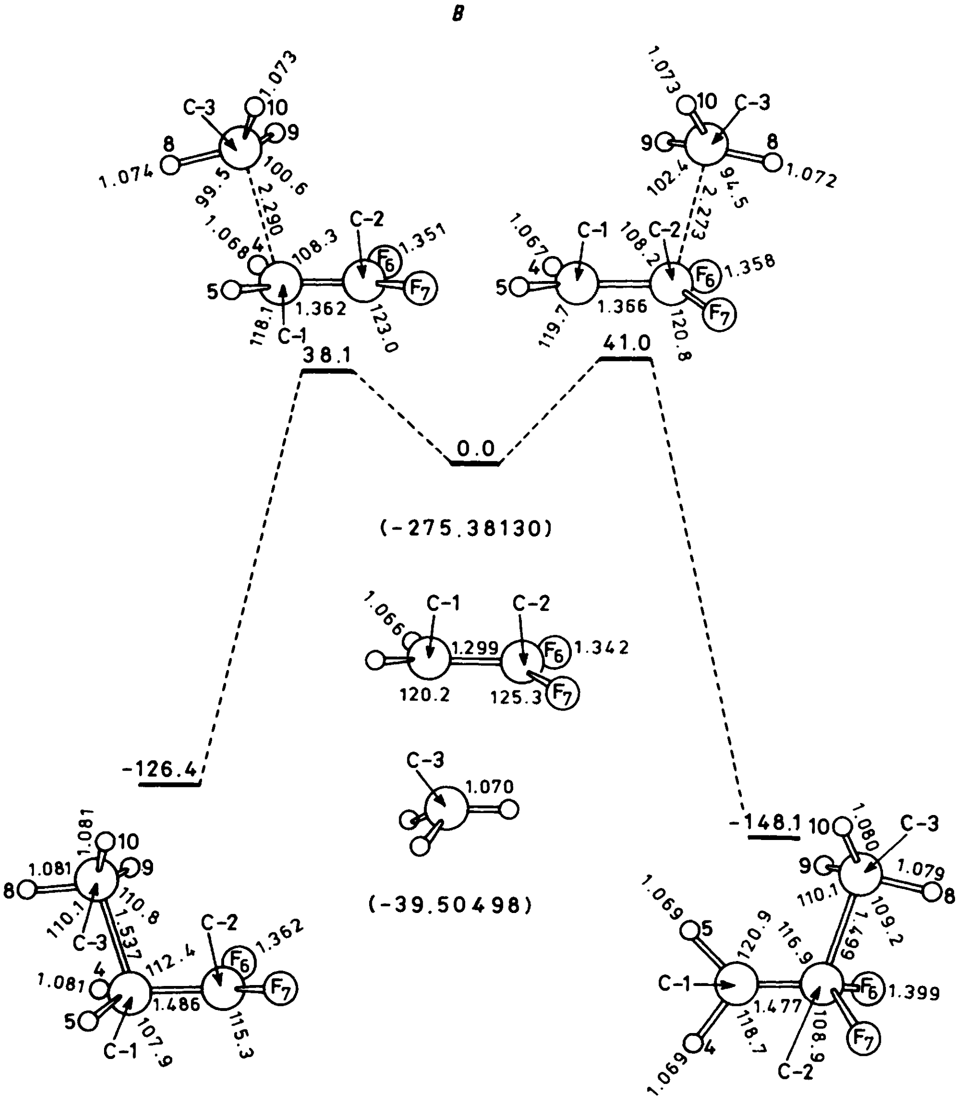

Figure 1 (*continued*)

Table 3. Harmonic frequencies computed at the 4-31G level (in cm^{-1}) for the transition states of the additions of CH_3 to ethylene (from ref. 23) and fluoroethenes

TSE:	475i; 109, 258, 405, 610, 619, 848, 887, 933, 1 028, 1 072, 1 299, 1 364, 1 579, 1 582, 1 619, 1 677, 3 239, 3 298, 3 310, 3 375, 3 388, 3 400, 3 405
TS1F1:	488i; 103, 128, 294, 483, 587, 608, 661, 890, 936, 1 012, 1 064, 1 246, 1 353, 1 526, 1 576, 1 581, 1 647, 3 240, 3 335, 3 392, 3 404, 3 424, 3 441
TS2F1:	543i; 99, 200, 290, 479, 573, 623, 634, 815, 905, 984, 1 058, 1 229, 1 346, 1 519, 1 572, 1 577, 1 639, 3 242, 3 339, 3 396, 3 406, 3 411, 3 444
TS1F2:	482i; 92, 114, 122, 425, 429, 517, 568, 577, 843, 849, 850, 1 022, 1 089, 1 422, 1 539, 1 571, 1 576, 1 666, 3 245, 3 366, 3 404, 3 412, 3 471
TS2F2:	549i; 81, 187, 198, 363, 430, 513, 589, 593, 604, 817, 889, 1 004, 1 051, 1 391, 1 511, 1 565, 1 567, 1 645, 3 250, 3 366, 3 413, 3 420, 3 477
TS1F3:	456i; 77, 98, 101, 227, 267, 407, 470, 516, 538, 624, 791, 942, 959, 1 215, 1 351, 1 471, 1 560, 1 566, 1 676, 3 250, 3 417, 3 422, 3 467
TS2F3:	489i; 77, 100, 175, 227, 278, 340, 469, 521, 540, 627, 667, 904, 952, 1 228, 1 334, 1 448, 1 561, 1 562, 1 662, 3 252, 3 420, 3 425, 3 475

C_2H_4, which, in turn, are only slightly modified at the TS.[23,51] On increasing the number of fluorine atoms in the olefin, new low-frequency modes appear (see Table 3), which mix with the five previous ones. As a consequence several frequencies are modified and it is no longer possible to isolate single contributions.

The potential energy barriers computed at the 4-31G level (Figure 1 and Table 4) correctly reproduce the experimental trends concerning both the overall reactivity and the regioselectivity in the methyl addition to fluoroethenes. Inclusion of non-potential energy (NPE) terms does not significantly alter the situation, although some peculiar trend is apparent (see Table 4). Thus, the ΔT terms slightly increase with the total number of fluorine atoms, but are completely insensitive to the distribution of the fluorine atoms between the two carbon atoms of the olefin. At the same time, ΔZPE decreases with the total number of fluorine atoms, but is essentially sensitive to the constitution of the attacked carbon atom. As a result the difference between CH_2,CHF and CHF,CF_2 edges is nearly constant and equal (*ca.* 0.8 kJ mol^{-1}); furthermore, the difference between the CH_2 and CF_2 edges is exactly the sum of the two previous differences. As a matter of fact the overall Δ(NPE) is nearly constant for a given number of fluorine atoms on the attacked centre, going from 6.7 for CH_2 to 6.0 for CHF,

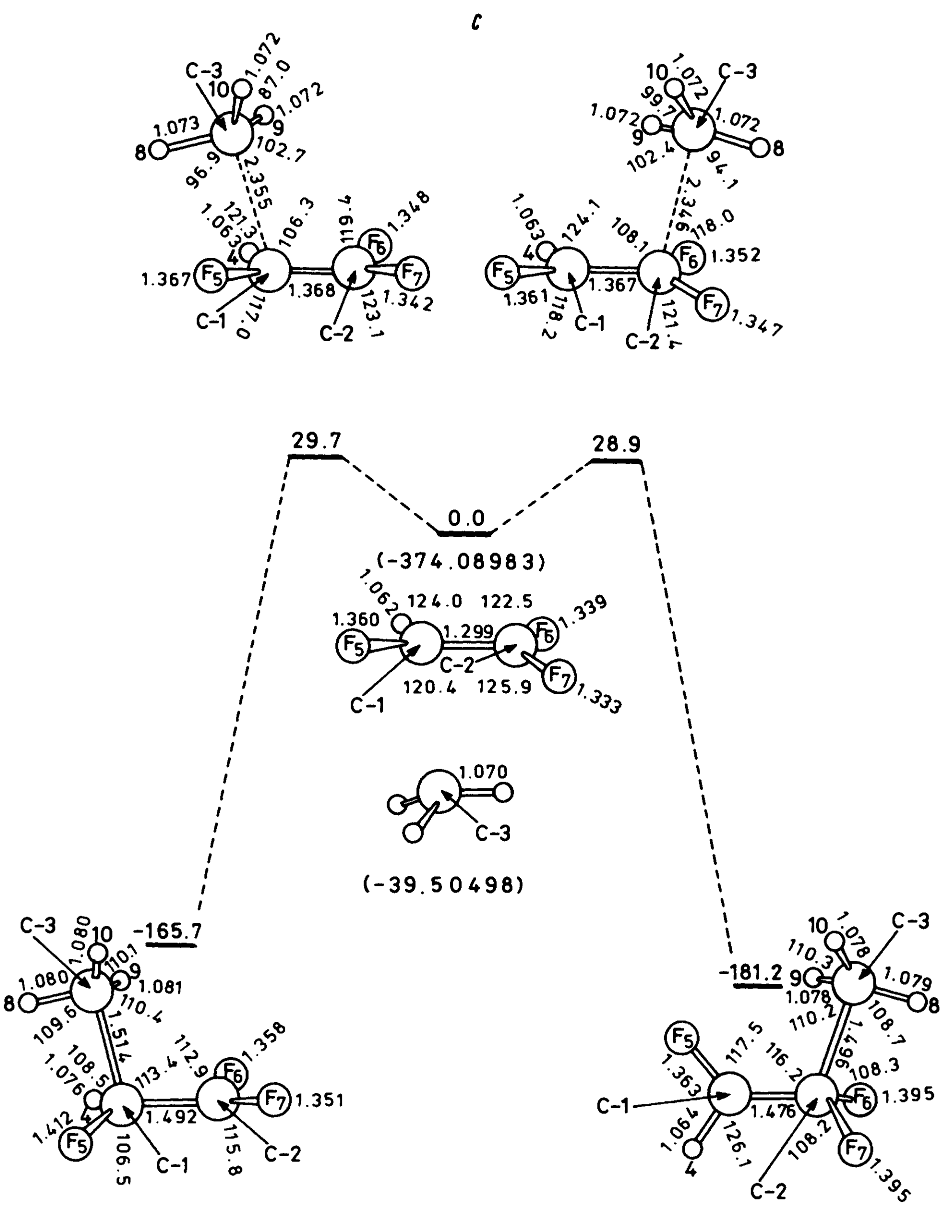

Figure 1 (*continued*)

Table 4. Calculated kinetic parameters at 160 °C ($RT = 3.6$ kJ mol^{-1}) for the addition of methyl radicals to ethylene and fluoroethenes. The different symbols are defined in the text

Property	$CH_2=CH_2$	$CH_2=CHF$ on C-1	$CH_2=CHF$ on C-2	$CH_2=CF_2$ on C-1	$CH_2=CF_2$ on C-2	$CHF=CF_2$ on C-1	$CHF=CF_2$ on C-2
E_r[a]	−95.0	−100.0	−109.6	−126.4	148.1	−165.7	−181.2
$\Delta E^{\ddagger}$[a]	36.4	37.7	41.8	38.1	41.0	29.7	28.9
Δ(ZPE)[a]	7.5	6.7	5.9	5.4	3.8	3.8	2.9
$\Delta T'$[a]	−1.0	0.0	0.0	1.3	1.5	2.3	2.4
ΔS[b]	−118.6	−127.7	−131.2	−116.1	−118.9	−117.1	−120.0
E_a[a]	46.5	48.0	51.3	48.4	49.9	39.4	37.8
log(A)	9.2	8.7	8.5	9.3	9.2	9.3	9.1
k_1/k_2[c]	1	3.4 (5)		2.0		0.9 (0.5)	

[a] In kJ mol^{-1}. [b] In J mol^{-1} K^{-1}. [c] Orientation rates; experimental values from ref. 1*a* are given in parentheses.

and to 5.3 kJ mol^{-1} for CF_2. On the other hand the reaction entropies favour the attacks at the less substituted centres, so that, as a final result, the reaction rates are essentially determined by the potential energy barriers.

4. *Mechanistic Considerations.*—The relative importance of the various interactions in determining the overall reactivity of different substrates and the regioselectivity can be analysed with reference to the energy components given in Table 5.

Let us first consider the intramolecular deformation of the substrate ($E^S_{def.}$) and of the radical ($E^R_{def.}$), which represent the energies to be furnished to the system in order to deform each of the isolated fragments from equilibrium geometry to geometry at the TS. This term represents in some way a measure of the geometry modifications described above. The contribution to $E_{def.}$ of the methyl fragment is always very small and does not influence the regioselectivity. It is however noteworthy that the variation in $E^R_{def.}$ parallels the increase in reaction

Table 5. Energy-component analysis (in kJ mol^{-1}) for the transition states of the addition reactions of CH_3 to ethylene (from ref. 23) and fluoroethenes[a]

		C_2H_3F		$C_2H_2F_2$		C_2HF_3	
	C_2H_4	on C-1	on C-2	on C-1	on C-2	on C-1	on C-2
$\Delta E^{\ddagger}$ [b]	36.4	37.7	41.8	38.1	41.0	29.7	28.9
$E^{S}_{def.}$	26.8	29.3	37.7	38.1	52.7	46.1	49.4
$E^{R}_{def.}$	6.7	6.3	6.2	5.0	4.6	3.4	3.3
$E_{int.}$ [c]	2.9	2.1	−2.1	−5.0	−16.3	−19.7	−23.8
E_{es}	−73.2	−76.6	−78.7	−65.2	−66.2	−54.0	−54.3
E_{pl}	−6.3	−6.6	−8.4	−4.6	−7.5	−4.2	−5.4
$E_{ct}(S \rightarrow R)$	−25.9	−26.4	−27.2	−21.3	−20.5	−17.2	−16.3
$E_{ct}(R \rightarrow S)$	−26.8	−27.2	−29.7	−22.6	−25.9	−19.2	−20.9
E_{ex}	184.1	186.2	190.0	156.4	154.0	124.6	122.5
E_{mix}	−49.0	−47.3	−48.1	−47.7	−50.2	−49.7	−49.4
ΔE_{φ} [d]		3.5		6.2		2.4	
ΔE_{def}		8.3		14.2		3.4	
ΔE_{int} [d]		−4.2		−11.3		−4.1	

[a] Negative values correspond to stabilising interactions. [b] $\Delta E^{\ddagger} = E^{S}_{def.} + E^{R}_{def.} + E_{int.}$. [c] $E_{int.} = E_{es} + E_{pl} + E_{ct}(S \rightarrow R) + E_{ct}(R \rightarrow S)$ $E_{ex} + E_{mix}$. [d] Energy differences between the two ends of the same substrate.

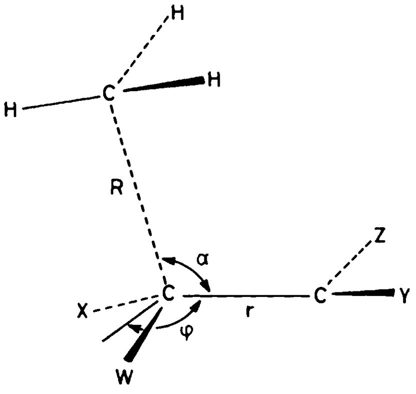

Figure 2.

energies. The essential contribution to the deformation energy comes from the olefin and this contribution provides a strong discrimination between the two possible attacks on a given substrate, strongly favouring the less substituted edge. The largest difference is obtained, of course, for 1,1-difluoroethene, but the difference is much larger in fluoroethene than in trifluoroethene. These large variations of $E^{S}_{def.}$ are quite surprising if one considers the overall similarity of the different transition states. Although the deformation undergone by the olefin moiety in passing from the reactants to the transition state cannot be represented by changes in a single geometrical parameter, it remains nevertheless true that the out-of-plane bending (φ) of the attacked centre (see Figure 2) gives the main contribution. In this respect it is noteworthy that the energy required to bring the CXY plane out of the equilibrium geometry increases in going from CH_2 to CHF and to CF_2. This effect is shown in Table 5, where we also report, for the two ends of fluoroethenes F1, F2, and F3, the deformation energy (ΔE_{φ}) calculated as the energy difference (at the 4-31G level) between fully optimized geometries at $\varphi = 0°$ and $\varphi = 15°$. It is apparent that, for a given substrate, ΔE_{φ} is larger at the most fluorinated end. We can therefore conclude that the larger deformation energy $E^{S}_{def.}$ associated to the attack to the most substituted carbon atom is mainly due to the greater energy required to pyramidalize this centre.

A correlation between $E_{def.}$ and the localization of the transition state along the reaction path was suggested in ref. 21 ('the smaller the $E_{def.}$ value is, the earlier is the transition state') because small deformation energies should be associated with strong inter-fragment interactions, which, in turn, lead to early transition states. The computations of refs. 20 and 21 actually show the limitations of this point of view: in fact *for a given substrate* smaller $E_{def.}$ values are generally associated with more exothermic processes (system vinylamine + H and F2 + H; the system vinylborane + H which does not follow this trend represents an extreme situation). In methyl additions to fluoroethenes, higher deformation energies of the substrates are found for the more exothermic processes, thus the relation with the earliness character of the transition states is partly lost since R and $E^{R}_{def.}$ obey the 'thermodynamic control,' but $E^{S}_{def.}$ is mainly related to the 'intrinsic easiness' of deformations at the attacked carbon atom.

The interaction energy $E_{int.}$ ($E_{int.} = \Delta E^{\ddagger} - E_{def.}$) well reproduces the reaction energies of the different reaction processes: in fact the stabilizing effect of this contribution increases with the total number of fluorine atoms and, for a given substrate, with the number of fluorine atoms at the attacked centre. The stabilization effect previously mentioned for product radicals is also operative (although to a lower extent) in the transition states. Thus the regioselectivity of methyl addition is determined by a delicate balance between $E_{int.}$ (which favours the attack at the more fluorinated carbon atom) and $E_{def.}$ (which favours the attack at the less fluorinated carbon atom). It is noteworthy in this connection that the difference in $E_{int.}$ values between CH_2–CHF edges from one side and CHF–CF_2 from the other is essentially identical, but the difference in $E_{def.}$ is much larger in the former case (see Table 5); as a consequence, the methyl radical preferentially attacks CH_2 and CF_2 centres rather than CHF ones. Besides, the results of F2 show that CH_2 edges are more reactive than CF_2 ones since the regioselective control of $E_{def.}$ prevails. On these grounds we can also understand the progressive variation of regioselectivity upon progressive fluorination of CH_3: in fact the $E_{def.}$ regioselective control is essentially unmodified, but the relative strengths of the incipient C–C bonds are reversed (see section 2). This interpretation is also in agreement with the variations of relative reactivities in going from C_2H_4 to C_2F_4: in fact the ratio of the rate constants $k(C_2F_4)/k(C_2H_4)$ is 9.5 when the attacking radical is CH_3, but becomes 0.1 when the attacking radical is CF_3.[1b] Finally in the case of hydrogen attack the C–H bond strengths are much less sensitive to fluorine substitution[52] and the regioselectivity is once again determined by $E_{def.}$.

Let us now consider the different contributions to the interaction energy $E_{int.}$ The exchange term E_{ex} is large and represents between 3 and 5 times the energy barrier $\Delta E^{\ddagger}$; the importance of the exchange repulsion demands its inclusion in any reasonable theoretical model. The electrostatic contribution E_{es} is more stabilizing than the charge-transfer interaction E_{ct}. This latter contribution can be decomposed into a term corresponding to electron transfer from the substrate to the radical (indicated by S→R) and a back-transfer term (indicated by R→S); for all the reactions studied here the back-ct contribution is the most important. It should be also noted, that, for a given substrate, the difference between the back and forward ct is larger for the transition state obtained upon addition of CH_3 to the more fluorinated carbon atom; in fact the ratio (back-ct):(forward-ct) is 1.03 and 1.09 in TS1F1 and TS2F1; 1.06 and 1.26 in TS1F2 and TS2F2; and 1.12 and 1.28 in TS1F3 and TS2F3. From this point of view we can conclude that the methyl radical acts as a *nucleophile* with respect to all the substrates. From the same point of view it can be observed that the hydrogen atom acts as an *electrophile* with respect to F2;[20] in fact the ratio (back-ct):(forward-ct) is 0.82 and 0.98 for attack at C-1 and C-2, respectively.

The values of Table 5 do not allow a clear-cut analysis of the variations of the different contributions to $\Delta E^{\ddagger}$ for the two possible attacks on a given substrate for a number of reasons: (i) the difference in $E_{\text{int.}}$ for the attack at C-1 or C-2 is always quite small; (ii) the absolute values of the different contributions are strongly dependent on the inter-fragment distance R (the smaller R is, the larger the absolute values are); (iii) the absolute values of the different contributions depend also on the extent of molecular deformation.[20] We therefore limit ourselves to a comparison of the relative weights of stabilizing ($E_{\text{st}} = E_{\text{es}} + E_{\text{pl}} + E_{\text{ct}}$) and destabilizing ($E_{\text{ds}} = E_{\text{ex}}$) interactions. The ratio $E_{\text{st}}/E_{\text{ds}}$ is 0.72 (TSE), 0.73 (TS1F1), 0.76 (TS2F1), 0.73 (TS1F2), 0.78 (TS2F2), 0.76 (TS1F3), and 0.79 (TS2F3): the ratio is thus always larger, for a given substrate, when the methyl radical attacks the C-2 atom. It is noteworthy in this connection that in the case of F2 the same ratio is 0.74 and 0.70 for the attack of H to C-1 and C-2, respectively (computed by the data of Table 5 in ref. 20). Since E_{st} represents the so-called 'polar term'[21] we obtain in this way a 'measure' of the difference between the polarities of the radicals H and CH_3 in the addition to F2. Our results suggest, however, that the increase of the abovementioned ratio when the attack of CH_3 occurs on the more substituted carbon atom is essentially due to a reduction of the exchange repulsion.

Conclusions

The main results of our study can be summarized as follows: (1) entropy effects are not responsible for the inversion of the stereoselectivity in the case of F3. (2) The relative ease in the deformation of the ends of a given substrate plays a significant role in determining the preferred direction of the attack; $E_{\text{def.}}$ is surely the determining factor in the case of monofluorinated olefins. (3) Fluorine atoms exerts a stabilizing effect on the incoming C–C bond; this effect allows us to explain the different regioselectivities in the attacks of CH_3 and CF_3 to trifluoroethene. (4) We think finally that this study will allow a quantitative defination of the 'polar' and 'steric' effects invoked by Tedder[1b] to explain the regioselectivity in the additions of CH_3 to F1 and F3.

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References

1 J. M. Tedder and J. C. Walton, (*a*) *Acc. Chem. Res.*, 1976, **9**, 183; (*b*) *Tetrahedron*, 1980, **36**, 701; (*c*) C. Ruchart, *Top. Curr. Chem.*, 1980, **88**; 1; (*d*) A. L. J. Beckwith, *Tetrahedron*, 1981, **37**, 3073.

2 J. M. Tedder, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 401.

3 B. Giese, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 753.

4 P. M. Scott and K. R. Jennings, *J. Phys. Chem.*, 1969, **73**, 1521.

5 J. N. Cape, A. Greig, J. M. Tedder, and J. C. Walton, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 592.

6 (*a*) J. M. Tedder, J. C. Walton, and K. D. R. Winton, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 1866; (*b*) H. C. Low, J. M. Tedder, and J. C. Walton, *ibid.*, 1976, **72**, 1707.

7 J. M. Tedder and J. C. Walton, *Adv. Phys. Org. Chem.*, 1978, **16**, 51.

8 R. Ponec, J. Málek, W. Kühnel, and E. Gey, *Theochem.*, 1984, **110**, 293.

9 R. Ponec and J. Málek, *Theochem.*, 1982, **88**, 295.

10 J. P. Poblet, E. Canadell, and T. Sordo, *Can. J. Chem.*, 1983, **61**, 2068.

11 S. Nagase and C. W. Kern, *J. Am. Chem. Soc.*, 1979, **101**, 2544.

12 S. Nagase, T. Fueno, and K. Morokuma, *J. Am. Chem. Soc.*, 1979, **101**, 5849.

13 W. L. Hase, R. J. Wolf, and C. S. Sloane, *J. Chem. Phys.*, 1979, **71**, 2911.

14 S. Kato and K. Morokuma, *J. Chem. Phys.*, 1980, **72**, 206.

15 S. Nagase and C. W. Kern, *J. Am. Chem. Soc.*, 1980, **102**, 4513.

16 W. L. Hase, D. M. Ludlow, R. J. Wolf, and T. J. Schlick, *J. Phys. Chem.*, 1981, **85**, 958.

17 W. L. Hase and H. B. Schlegel, *J. Phys. Chem.*, 1982, **86**, 3901.

18 L. B. Harding, A. F. Wagner, J. M. Bowman, G. C. Schatz, and K. Christoffel, *J. Phys. Chem.*, 1982, **86**, 4312.

19 H. B. Schlegel and C. Sosa, *J. Phys. Chem.*, 1984, **88**, 1141.

20 R. Arnaud, Y. Ellinger, R. Subra, and J. Douady, *Theochem.*, 1984, **110**, 203.

21 F. Delbecq, D. Ilavsky, Nguyen Trong Anh, and J. M. Lefour, *J. Am. Chem. Soc.*, 1985, **107**, 1623.

22 D. T. Clark, I. W. Scanlan, and J. C. Walton, *Chem. Phys. Lett.*, 1978, **55**, 102.

23 R. Arnaud, V. Barone, S. Olivella, and A. Solé, *Chem. Phys. Lett.*, 1985, **118**, 573.

24 After the completion of this study, we became aware of an independent theoretical work on the addition of methyl to mono- and tri-fluoroethene by Canadell and co-workers.

25 K. Morokuma, *J. Chem. Phys.*, 1971, **55**, 1236; K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, 1976, **10**, 326.

26 J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, R. L. Kahn, and J. A. Pople, *Quantum Chemistry Program Exchange*, 1980, **13**, 406.

27 R. Ditchefield, W. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.

28 H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214.

29 M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, 1977, **99**, 7822.

30 G. Fogarasi and P. Pulay, *Annu. Rev. Phys. Chem.*, 1984, **35**, 191.

31 G. Leroy, *Adv. Quantum Chem.*, 1985, **17**, 1.

32 K. J. Laidler, 'Chemical Kinetics,' McGraw-Hill, New York, 1965, p. 85.

33 P. D. Pacey, *J. Chem. Educ.*, 1981, **58**, 612, and references therein.

34 R. Arnaud, V. Barone, S. Olivella, N. Russo, and A. Solé, *J. Chem. Soc., Chem. Commun.*, 1985, 1331.

35 R. D. Bach and G. J. Wolber, *J. Am. Chem. Soc.*, 1984, **106**, 1401.

36 D. J. DeFrees, B. A. Levi, S. K. Pollack, W. J. Hehre, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, 1979, **101**, 4085.

37 D. J. DeFrees, K. Ragavachary, H. B. Schelgel, and J. A. Pople, *J. Am. Chem. Soc.*, 1982, **104**, 5576.

38 L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, Jr., *J. Chem. Phys.*, 1965, **42**, 2683; K. Kuchitsu, *ibid.*, 1966, **44**, 906.

39 J. L. Carlos, Jr., R. R. Karl, Jr., and S. H. Bauer, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 177.

40 A. Yokozeki and S. H. Bauer, *Top. Curr. Chem.*, 1975, **53**, 71.

41 J. L. Duncan, D. C. McKean, and P. D. Mallinson, *J. Mol. Spectrosc.*, 1973, **45**, 221.

42 B. Bak and D. Christensen, *Spectrochim. Acta*, 1958, **12**, 355; 1959, **13**, 120.

43 W. F. Edgell and W. E. Bird, *J. Chem. Phys.*, 1949, **17**, 740; J. S. Scherer and J. Overend, *J. Chem. Phys.*, 1960, **32**, 1720.

44 D. E. Mann, N. Acquista, and E. K. Plyler, *J. Chem. Phys.*, 1954, **22**, 1586.

45 J. Pacansky and J. Bargon, *J. Am. Chem. Soc.*, 1975, **97**, 6896.

46 D. C. Smith, J. R. Nielsen, and H. H. Classen, *J. Chem. Phys.*, 1950, **18**, 326.

47 Average among the values reported by D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125.

48 J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, N.Y., 1970.

49 W. Tsang, *J. Am. Chem. Soc.*, 1985, **107**, 2872.

50 N. D. Epiotis, W. R. Cherry, S. Shaik, R. L. Yates, and F. Bernardi, *Top. Curr. Chem.*, 1977, **70**, 199.

51 E. Canadell, J. M. Poblet, and S. Olivella, *J. Phys. Chem.*, 1983, **87**, 424.

52 (*a*) W. H. Fligare, *J. Mol. Spectrosc.*, 1968, **25**, 365; (*b*) J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, 1964, **20**, 523; (*c*) V. Galasso, G. De Alti, and G. Costa, *ibid.*, 1965, **21**, 669.

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