Mechanism of Addition of Fluoromethyl Radicals to Fluoroethylenes

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The self-consistent charge and configuration method for subsystems (SCCCMS), charge sensitivity analysis, and our new scheme for energy partitioning were applied to discuss the mechanism of addition of fluoromethyl radicals to fluoroethylenes. A hybrid density functional method, i.e., the combination of Becke's three-parameter functional and the Perdew/Wang 91 gradient-corrected functional, was used in the calculations with the 6-31G* basis set. Charge sensitivity characteristics (chemical potentials and hardnesses) of the reactants have been obtained. Chemical potentials clearly showed that alkenes act as donors of electrons (bases), while radicals act as acceptors (acids). The systems "electronic activation energies" were decomposed into deformation, electrostatic, polarization, charge-transfer, and exchange components. Steric effect was identified with the sum of deformation and exchange energies, while polar effect was related to the sum of electrostatic, charge-transfer, and polarization contributions. A correlation between the magnitude of polar effect and inter-reactant distance in transition states was found. It has been demonstrated that the anomaly in regioselectivity in methyl or fluoromethyl radical addition to trifluoroethylene is understandable as an electrostatically controlled process.

1. Introduction

Free radical addition reactions are more complicated than ionic processes. It is difficult to find simple rules explaining experimental observations for radical addition reactions.[1−3] For example, the orientation in free radical addition to unsymmetrical alkenes strongly depends on the type of radical and alkene, while electrophilic addition to alkenes usually obeys the Markovnikov rule. Tedder has summarized the influences of substituents on radical addition reactions in the following empirical rules:[2] (i) preferred orientation of addition of a free radical to monosubstituted alkenes will invariably be to the unsubstituted end of double bond; (ii) substituents with C−C π-orbitals enhance the rate of addition at the remote end of the double bond, while nonbonding pairs of electrons have only a very small "resonance effect"; (iii) polarity can have a major effect on the overall rate of addition of radicals to alkenes; (iv) the orientation of radical addition to polysubstituted ethylenes is controlled principally by the degree of steric compression associated with forming the new bond; (v) polarity can influence the magnitude of the regioselectivity for addition to polysubstituted ethylenes. Of similar nature are the rules of Giese.[3] He has concluded that steric and polar effects play an essential role in radical addition to mono- and polysubstituted ethylenes.

Many theoretical studies have been carried out for radical addition reactions to alkenes.[4−39] Energy profiles for radical addition to monosubstituted ethylenes were found to be qualitatively understandable by taking into account a few principal valence-bond configurations. Salem et al.[7] devised a simple three-center three-electron model. Recently, Wong and coworkers[31−33] applied the curve-crossing model[40] to analyze the mechanism of radical addition reactions. The authors have revealed to what extent the excited configurations, e.g., the charge-transfer configurations, are mixed to the ground-state reaction profile. In addition, the role of polar effects has also been investigated.

The energy decomposition scheme developed by Kitaura and Morokuma[41] offers another insight into the mechanism of the radical addition reactions. Interaction energy between radical and alkene was decomposed into several components. For the reaction of methyl radical with mono-, di-, and trifluoroethylene, electrostatic and charge-transfer components, as well as polarization contribution, facilitate addition to the more fluorinated site.[21] Polarization contribution is insignificant, as compared with the other energy components.[9,13,20,21,28] However, each energy component does not directly correspond to intuitive concepts, such as steric and polar effects.

From the point of view of frontier molecular orbital (FMO) theory,[42] SOMO (singly occupied molecular orbital)−LUMO (lowest unoccupied molecular orbital) or SOMO−HOMO (highest occupied molecular orbital) interaction is important to understand radical addition reactions. Poblet et al.[17] compared the shapes of SOMO's of supermolecular systems with those of HOMO's/LUMO's of alkenes. They have shown that SOMO−HOMO interactions are predominant for methyl radical addition to monosubstituted ethylenes and 1,1′-difluoroethylene.

The approaches mentioned above can frequently rationalize experimental observations for radical reactions. However, all of them fail to provide a convincing interpretation toward the regioselectivity in methyl or fluoromethyl radical addition to trifluoroethylene ($^{\bullet}CH_3/C_2HF_3$ or $^{\bullet}CH_2F/C_2HF_3$ system). In contrast to the general rule predicting preferential addition to the less substituted carbon atom, addition of $^{\bullet}CH_3$ and $^{\bullet}CH_2F$ radicals preferentially occurs at the CF_2 end of trifluoroethylene. Even more recent investigations[37] based on Fukui function[43−44] cannot rationalize this anomaly in regioselectivity.

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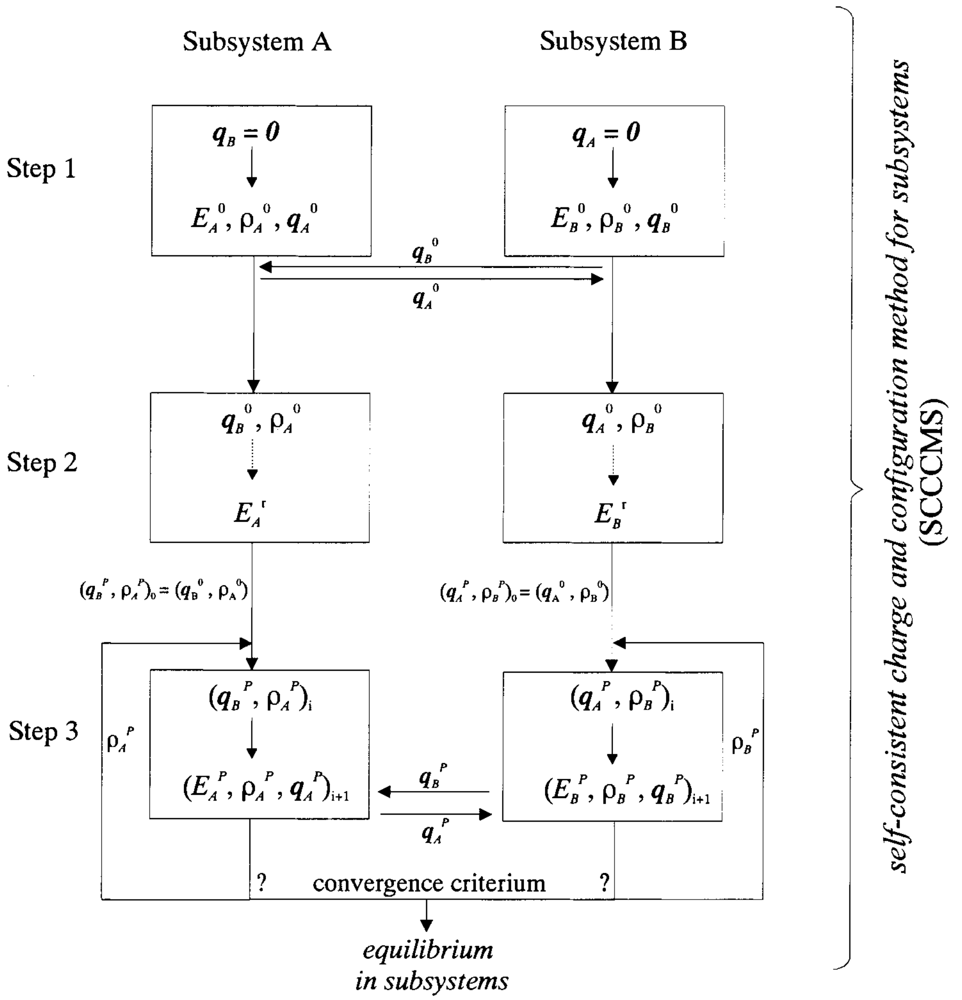

Figure 1. Schematic representation of constrained calculations. For reasons of simplicity, the whole iteration procedure via orbitals or N-electron wave functions is represented by the $\rho \rightarrow E$ symbol. If the solid arrow is replaced by dashed one, then density and charges are frozen. Convergence criterium in step 3 is as follows $|(E_A^P + E_B^P - \sum_{\alpha\in A}\sum_{\beta\in B} q_\alpha^P q_\beta^P / r_{\alpha\beta})_i - (E_A^P + E_B^P - \sum_{\alpha\in A}\sum_{\beta\in B} q_\alpha^P q_\beta^P / r_{\alpha\beta})_{i-1}| \langle \epsilon$, where i counts iterations and ϵ is a small positive value (0.000 001 hartree).

Recently, we have applied density functional methods[45] to analyze energy profiles for the following class of radical addition reactions[39]

$$^{\bullet}CH_{3-n}F_n + C_2H_{4-m}F_m \rightarrow \text{adduct radical} \qquad (1)$$

where $n = 0$, 1, 2, or 3 and $m = 0$, 1, 2, 3, or 4, respectively [starting from addition of methyl radical to ethylene ($^{\bullet}CH_3/C_2H_4$ system) up to that of trifluoromethyl radical to tetrafluoroethylene ($^{\bullet}CF_3/C_2F_4$ system)]. We showed that Becke's three-parameter functional[46] with the Perdew/Wang 91 gradient-corrected correlation functional[47] (B3PW91) reproduced adequately experimentally measured activation energies for the reactions in eq 1. More recently, we have developed a new scheme[48] for analyzing interaction between reactants. Decomposition of interaction energy in our scheme is based on charge sensitivity concepts[49] and the self-consistent charge and configuration method for subsystems (SCCCMS). We have applied the scheme to investigate the mechanism of all reactions in eq 1. In this paper, we will describe the results of our analysis. In particular, detailed discussion on the factors responsible for the regiochemistry in radical addition, including interpretation of the anomaly in regioselectivity for $^{\bullet}CH_3/C_2HF_3$ and $^{\bullet}CH_2F/C_2HF_3$ systems, will be presented.

2. Method

We will describe now our procedure, which was used to investigate the mechanism of the radical addition reactions in eq 1. The procedure provides a qualitative interpretation tool allowing us to understand the nature of interactions between the reactants. Similarly, as in Kitaura and Morokuma's scheme,[41] we will decompose the system interaction energy. Our scheme of energy partitioning will exactly follow the hypothetical stages of the charge reorganization accompanying the chemical reaction:[49]

step 1, the separated (noninteracting, infinitely distant) reactants, $M^0 = A^0 + B^0$;

step 2, the "rigid" (r) interacting reactants, $M^r = (A^0|B^0)$;

step 3, the polarized (P), mutually closed reactants, $M^P = (A^P|B^P)$;

step 4, the mutually opened reactants, $M = (A \cdots B)$.

Hereafter, M represents the whole molecular system, while A and B represent subsystems (reactants). Parentheses denote interacting subsystems; solid and dotted lines between A and B correspond to mutually closed and opened reactants, respectively. The crucial point of the scheme is connected with step 3. In the next section, we present a simple calculation scheme leading to polarized reactants.

2.1. The Self-Consistent Charge and Configuration Method for Subsystems (SCCCMS). Figure 1 shows a way of achieving the state in which the reactants are mutually polarized (intra-reactant equilibrium, step 3). The reactants A and B are closed subsystems, i.e, charge transfer between them is not allowed. We assume that the presence of the reaction partner can be approximated by point charge distribution. Namely, calculations for the reactant A are performed with the background charges characterizing B ($\mathbf{q}_B = \{q_1^B, q_2^B, ...\}$) and vice versa. In the present work, the geometries of the reactants were fixed to those of the transition state and the point charges were located at the positions of the nuclei of the reaction partner. The initial conditions are chosen in such a way that steps 1 and 2 are naturally included into the computational scheme.

In step 1, the interaction between A and B is turned off. It means that vectors grouping atoms-in-molecules charges are set to zero ($\mathbf{q}_A = \mathbf{0}_A$ and $\mathbf{q}_B = \mathbf{0}_B$). Thus, we obtain energies (E_A^0, E_B^0) and electron densities (ρ_A^0, ρ_B^0) of isolated reactants. In addition, the charge distributions corresponding to the electron densities are computed according to the assumed population analysis scheme, i.e., Mulliken charges[50] in the present study. In step 2, the electron densities and point charges obtained in step 1 are frozen. The energy of a given reactant is calculated in the presence of the point charges characterizing the reaction partner. The obtained energies describe the rigid, interacting reactants (E_A^r, E_B^r). Finally (step 3), we consider polarization effect. Electron densities and charge distributions of both subsystems are allowed to relax. Each SCF run, for reactant A, is performed in the presence of the point charges characterizing the reaction partner B. As a result, a new electron density of A is obtained. The same strategy is applied for reactant B. The modified electron densities and point charges derived from them are used in the next iteration. Iterations are continued until electron densities and point charges become self-consistent. As a final result, we obtain the energies (E_A^P, E_B^P) and electron densities (ρ_A^P, ρ_B^P) of mutually polarized reactants. We call this constrained calculational scheme the *self-consistent charge and configuration method for subsystems* (SCCCMS).

2.2. Charge Sensitivity Parameters. In hypothetical steps of charge reorganization, the molecular system (M) is seen either as one unit (supermolecule) or as composed from two subunits (interacting reactants). For the constant external potential, the energy of the molecular system (M) depends only on the global number of electrons (N), $E_M = E_M(N)$. Change in the system energy due to chemical oxidation (reduction) can be approximated by the quadratic Taylor expansion[49,51]

$$E_M(N) = E_M^0 + \left(\frac{\partial E_M}{\partial N}\right)(N - N^0) + \frac{1}{2}\left(\frac{\partial^2 E_M}{\partial N^2}\right)(N - N^0)^2 \qquad (2)$$

where $E_M^0 = E_M(N^0)$. The first- and second-order derivatives are the global chemical potential (μ^M) and global hardness (η^M), respectively. If N^0 represents the number of electrons in a neutral system, then eq 2 has the following form

$$E_M(q) = E_M^0 - \mu^M q + \frac{1}{2}\eta^M q^2 \qquad (3)$$

where q is the charge of the system. Substituting M in eq 3 by A or B, the energies of separated (noninteracting) reactants are obtained.

Taking into account reactant resolution, we have to consider the energy surface, $E_M = E_M(N_A, N_B)$; here N_A and N_B represent the numbers of electrons in subsystems A and B. The quadratic Taylor expansion of E_M is[49]

$$E_M = E_M^0 + \left(\frac{\partial E_M}{\partial N_A}\right)_{N_B}(N_A - N_A{}^0) + \left(\frac{\partial E_M}{\partial N_B}\right)_{N_A}(N_B - N_B^0) + \frac{1}{2}\left(\frac{\partial^2 E_M}{\partial N_A{}^2}\right)_{N_B}(N_A - N_A^0)^2 + \frac{1}{2}\left(\frac{\partial^2 E_M}{\partial N_B^2}\right)_{N_A}(N_B - N_B^0)^2 + \left(\frac{\partial^2 E_M}{\partial N_A \partial N_B}\right)(N_A - N_A^0)(N_B - N_B^0) \qquad (4)$$

Here, we expand the energy around the numbers of electrons N_A^0 and N_B^0 characterizing neutral subsystems. The first- and second-order derivatives are the chemial potentials of the reactants and the elements of the condensed hardness matrix, respectively. Thus, we can rewrite eq 4 as follows

$$E_M = E_M^0 - \mu_A^M q_A - \mu_B^M q_B + \frac{1}{2}\eta_{AA}^M q_A^2 + \frac{1}{2}\eta_{BB}^M q_B^2 + \eta_{AB}^M q_A q_B \qquad (5)$$

where q_A and q_B are charges of the subsystems.

2.3. Energy Partitioning Scheme. We will now decompose the global (g) change in the system energy (overall interaction energy), $\Delta E \equiv E^g = E_M - (E_A + E_B)$. Here, E_M, E_A, and E_B are the energies of supermolecule (step 4) and reactants (A, B) at the *minimum energy structures* (MES). Since geometries of subsystems A and B in the supermolecule are different from those of the reactants at the MES, geometry deformation (DEF) contributon to E^g can be defined:

$$E^{DEF} = (E_A^0 + E_B^0) - (E_A + E_B) \qquad (6)$$

The next component of E^g is the electrostatic (ES) term

$$E^{ES} = (E_A^r + E_B^r - V_{qq}^r) - (E_A^0 + E_B^0) \qquad (7)$$

The additional component $V_{qq}^r = \sum_{\alpha\in A}\sum_{\beta\in B} q_\alpha^0 q_\beta^0 / r_{\alpha\beta}$ is introduced in order to eliminate electrostatic interactions that are doubly counted.

The quantities obtained in the final step of SCCCMS (step 3) allow one to calculate the polarization contribution to interaction energy

$$E^P = (E_A^P + E_B^P - V_{qq}^P) - (E_A^r + E_B^r - V_{qq}^r) \qquad (8)$$

The V_{qq}^P term is again introduced to omit double counting of electrostatic interactions between subsystems ($V_{qq}^P = \sum_{\alpha\in A}\sum_{\beta\in B} q_\alpha^P q_\beta^P / r_{\alpha\beta} \neq V_{qq}^r$).

The charge-transfer (CT) contribution to interaction energy is obtained from the following formula:[49]

$$E^{CT} = -(\mu_A^M - \mu_B^M)^2 / 2(\eta_{AA}^M + \eta_{BB}^M - 2\eta_{AB}^M) \qquad (9)$$

This expression can be derived from the Taylor expansion (eq 5) by searching for the minimum of E_M under the constraint of $dq_A = -dq_B$ (chemical potential equalization).

Let us introduce now the last component of interaction energy using the energy balance equation. Summing all distinguished contributions to the overall interaction energy, one has to introduce an additional term (E^{EX})

$$E^{DEF} + E^P + E^{ES} + E^{CT} + E^{EX} = E^g \qquad (10)$$

We called it exchange (EX) contribution. One should remember that depending on the calculational scheme [Hartree−Fock (HF),

TABLE 1: Chemical Potentials (μ^X) and Hardnesses (η^X) of the Reactants in the Global Minimum Structures [X = A (Radical) or B (Ethylene)[a] Obtained from Eq 3[b]

	radical				alkene						
system	$^{\bullet}CH_3$	$^{\bullet}CH_2F$	$^{\bullet}CHF_2$	$^{\bullet}CF_3$	C_2H_4	C_2H_3F	CH_2CF_2	$C_2H_2F_2$ (*cis*)	$C_2H_2F_2$ (*trans*)	C_2HF_3	C_2F_4
μ^X	−0.156	−0.134	−0.153	−0.180	−0.132	−0.118	−0.113	−0.112	−0.112	−0.108	−0.104
η^X	0.505	0.477	0.483	0.473	0.424	0.432	0.433	0.423	0.423	0.422	0.421

[a] All values are in atomic units. [b] The reported data are obtained from the least-squares fitting to eq 3 by using energies of neutral reactant, its anion, cation, and dication (q = 0, −1, 1, and 2).

post-HF, Kohn−Sham methods] it can also include part of correlation, and kinetic energy, as well as higher order interactions. We would like to mention that the E^{EX} contribution should be more sensitive on the basis set employed than other contributions, since it is calculated via the balance equation. Detailed analysis of the basis set effect in our scheme will be given elsewhere.[48]

During decomposition of the system energy, we have based on hypothetical stages of the charge reorganization accompanying the chemical reaction (steps 1−4). Constraints in our scheme are imposed on electron density, while in Kitaura and Morokuma's scheme[41] constraints are imposed on wave functions. The present model is very simple. Of course, one can extend it by modeling interactions between subsystems more rigorously.

2.4. Computational Details. All calculations were carried out using the Gaussian 94 suite of programs[52] on an IBM 6000. We carried out charge sensitivity analysis[49] on the isolated reactants (ethylenes and radicals) and on the transition states for the radical addition reactions (see eq 1). Moreover, to clarify predominant interactions between the reactants in the transition states, we employed our new scheme of energy partitioning. The electronic activation energies (E^g) were decomposed into deformation (DEF), electrostatic (ES), polarization (P), charge-transfer (CT), and exchange (EX) components. Each contribution was calculated according to eqs 6−10. In the present work, we employed the B3PW91/6-31G* computational level of theory because our previous work[39] showed that this computational level reproduced adequately activation energies for the radical addition reactions in eq 1. The geometries of the transition states were given in our previous paper.[39] Restricted and unrestricted wave functions were used for the calculations of closed and open shell species, respectively.

3. Results

The calculated chemical potentials and hardnesses are reported in Tables 1 and 2. Table 3 collects the results of energy partitioning for the transition state structures. Figure 2 shows the differences between activation energies (E^g) of transition states with the opposite orientation of a given radical toward the double bond in unsymmetrical ethylenes (entry B vs C, D vs E, and H vs I in Table 3). Figure 2 also includes each term of the energy-partitioning scheme. The negative value indicates that a given energy component favors radical addition to the less fluorinated site, while the positive value indicates the opposite tendency in regioselectivity.

3.1. Charge Sensitivity Characteristic of Reactants. Table 1 shows charge sensitivity parameters of the isolated ethylenes and radicals in global minimum structures. We obtained the values of μ^X and η^X given in the table by least-squares fitting to energies of neutral and charged reactants (see the footnote of Table 1). Regardless of fluoro-substitution patterns in ethylenes and in radicals, the chemical potentials (μ^X) of ethylenes were higher than those of radicals. Thus, ethylenes and radicals act as a base [B (electron donor)] and as an acid [A (electron acceptor)], respectively, which suggests that HOMO−SOMO interaction between the reactants will be dominant for all reactions in eq 1. This result is consistent with the findings of Poblet et al.[17] and Pross et al.[32] Furthermore, one can notice that successive fluorination increases the chemical potential of isolated ethylenes. However, a similar trend (substituent effect) was not seen in the chemical potentials of

TABLE 2: Charge Sensitivity Parameters[a] of the Reactants in the Transition States for the Addition of Radicals (A) to Ethylenes (B), M = (A|B)[b]

entry	system[c]	μ_B^M	μ_A^M	η_{BB}^M	η_{AA}^M	η_{AB}^M
A	$^{\bullet}CH_3/C_2H_4$	−0.114	−0.154	0.427	0.484	0.196
	$^{\bullet}CH_2F/C_2H_4$	−0.125	−0.141	0.417	0.460	0.192
	$^{\bullet}CHF_2/C_2H_4$	−0.128	−0.147	0.424	0.460	0.191
	$^{\bullet}CF_3/C_2H_4$	−0.135	−0.176	0.418	0.455	0.189
B	$^{\bullet}CH_3/\mathbf{CH_2}CHF$	−0.108	−0.156	0.419	0.474	0.197
	$^{\bullet}CH_2F/\mathbf{CH_2}CHF$	−0.114	−0.143	0.415	0.441	0.194
	$^{\bullet}CHF_2/\mathbf{CH_2}CHF$	−0.120	−0.150	0.414	0.459	0.191
	$^{\bullet}CF_3/\mathbf{CH_2}CHF$	−0.125	−0.179	0.415	0.445	0.186
C	$^{\bullet}CH_3/\mathbf{CHF}CH_2$	−0.110	−0.168	0.414	0.466	0.202
	$^{\bullet}CH_2F/\mathbf{CHF}CH_2$	−0.117	−0.151	0.410	0.436	0.198
	$^{\bullet}CHF_2/\mathbf{CHF}CH_2$	−0.124	−0.157	0.407	0.454	0.196
	$^{\bullet}CF_3/\mathbf{CHF}CH_2$	−0.128	−0.184	0.408	0.439	0.193
D	$^{\bullet}CH_3/\mathbf{CH_2}CF_2$	−0.104	−0.160	0.419	0.472	0.199
	$^{\bullet}CH_2F/\mathbf{CH_2}CF_2$	−0.111	−0.146	0.416	0.438	0.195
	$^{\bullet}CHF_2/\mathbf{CH_2}CF_2$	−0.115	−0.153	0.414	0.456	0.196
	$^{\bullet}CF_3/\mathbf{CH_2}CF_2$	−0.120	−0.182	0.416	0.442	0.190
E	$^{\bullet}CH_3/\mathbf{CF_2}CH_2$	−0.114	−0.179	0.405	0.460	0.204
	$^{\bullet}CH_2F/\mathbf{CF_2}CH_2$	−0.120	−0.162	0.401	0.430	0.201
	$^{\bullet}CHF_2/\mathbf{CF_2}CH_2$	−0.125	−0.165	0.398	0.448	0.200
	$^{\bullet}CF_3/\mathbf{CF_2}CH_2$	−0.132	−0.193	0.398	0.431	0.198
F	$^{\bullet}CH_3/\textit{cis}\text{-}C_2H_2F_2$	−0.107	−0.171	0.405	0.465	0.198
	$^{\bullet}CH_2F/\textit{cis}\text{-}C_2H_2F_2$	−0.113	−0.154	0.401	0.436	0.194
	$^{\bullet}CHF_2/\textit{cis}\text{-}C_2H_2F_2$	−0.118	−0.160	0.400	0.452	0.192
	$^{\bullet}CF_3/\textit{cis}\text{-}C_2H_2F_2$	−0.122	−0.188	0.400	0.438	0.189
G	$^{\bullet}CH_3/\textit{trans}\text{-}C_2H_2F_2$	−0.107	−0.170	0.405	0.467	0.197
	$^{\bullet}CH_2F/\textit{trans}\text{-}C_2H_2F_2$	−0.113	−0.153	0.401	0.436	0.194
	$^{\bullet}CHF_2/\textit{trans}\text{-}C_2H_2F_2$	−0.118	−0.159	0.399	0.453	0.192
	$^{\bullet}CF_3/\textit{trans}\text{-}C_2H_2F_2$	−0.122	−0.187	0.399	0.438	0.189
H	$^{\bullet}CH_3/\mathbf{CHF}CF_2$	−0.105	−0.173	0.404	0.465	0.196
	$^{\bullet}CH_2F/\mathbf{CHF}CF_2$	−0.110	−0.156	0.400	0.435	0.193
	$^{\bullet}CHF_2/\mathbf{CHF}CF_2$	−0.114	−0.163	0.399	0.452	0.192
	$^{\bullet}CF_3/\mathbf{CHF}CF_2$	−0.118	−0.191	0.399	0.436	0.189
I	$^{\bullet}CH_3/\mathbf{CF_2}CHF$	−0.111	−0.181	0.396	0.463	0.197
	$^{\bullet}CH_2F/\mathbf{CF_2}CHF$	−0.116	−0.163	0.393	0.432	0.194
	$^{\bullet}CHF_2/\mathbf{CF_2}CHF$	−0.119	−0.168	0.390	0.449	0.193
	$^{\bullet}CF_3/\mathbf{CF_2}CHF$	−0.124	−0.196	0.390	0.433	0.191
J	$^{\bullet}CH_3/C_2F_4$	−0.111	−0.184	0.395	0.474	0.184
	$^{\bullet}CH_2F/C_2F_4$	−0.110	−0.169	0.394	0.440	0.189
	$^{\bullet}CHF_2/C_2F_4$	−0.117	−0.172	0.388	0.451	0.188
	$^{\bullet}CF_3/C_2F_4$	−0.120	−0.199	0.391	0.439	0.186

[a] All values are in atomic units. [b] Data reported in the table are obtained from the least-squares fitting to Taylor expansion (eq 5) by taking into account energies of polarized subsystems with q_X = −1, 0, 1, and 2 (X = A or B). [c] Boldface letters represent the attacked reaction sites in unsymmetrical alkenes.

TABLE 3: Decomposition of the "Electronic Activation Energy" (E^{g}) into Deformation (E^{DEF}), Electrostatic (E^{ES}), Polarizational (E^{P}), Charge-Transfer (E^{CT}), and Exchange (E^{EX}) Components at the B3PW91 Level of Theory for the Addition of Fluoromethyl Radicals to Fluoroethylenes (Calculated for the Transition-State Structures)[a]

entry	system	E^{DEF}	E^{ES}	E^{P}	E^{CT}	E^{EX}	E^{g}
A	$^{\bullet}\mathrm{CH_3/C_2H_4}$	2.26	1.08	−0.34	−0.96	2.36	4.40
	$^{\bullet}\mathrm{CH_2F/C_2H_4}$	1.32	0.69	−0.28	−0.14	1.46	3.04
	$^{\bullet}\mathrm{CHF_2/C_2H_4}$	1.29	0.21	−0.12	−0.24	1.39	2.53
	$^{\bullet}\mathrm{CF_3/C_2H_4}$	0.96	−0.38	−0.33	−1.00	1.76	1.00
B	$^{\bullet}\mathrm{CH_3}/\mathbf{CH_2}\mathrm{CHF}$	2.51	1.46	−0.32	−1.48	2.47	4.63
	$^{\bullet}\mathrm{CH_2F}/\mathbf{CH_2}\mathrm{CHF}$	1.75	0.95	−0.11	−0.54	1.79	3.83
	$^{\bullet}\mathrm{CHF_2}/\mathbf{CH_2}\mathrm{CHF}$	1.45	0.01	−0.05	−0.58	2.02	2.85
	$^{\bullet}\mathrm{CF_3}/\mathbf{CH_2}\mathrm{CHF}$	1.12	−1.22	−0.30	−1.89	3.42	1.12
C	$^{\bullet}\mathrm{CH_3}/\mathbf{CHF}\mathrm{CH_2}$	3.88	0.22	−0.42	−2.20	4.67	6.15
	$^{\bullet}\mathrm{CH_2F}/\mathbf{CHF}\mathrm{CH_2}$	2.61	0.13	−0.15	−0.80	2.61	4.40
	$^{\bullet}\mathrm{CHF_2}/\mathbf{CHF}\mathrm{CH_2}$	2.36	−0.41	−0.05	−0.73	2.53	3.70
	$^{\bullet}\mathrm{CF_3}/\mathbf{CHF}\mathrm{CH_2}$	2.17	−1.04	−0.35	−2.11	4.34	3.01
D	$^{\bullet}\mathrm{CH_3}/\mathbf{CH_2}\mathrm{CF_2}$	3.00	1.81	−0.38	−2.03	2.76	5.15
	$^{\bullet}\mathrm{CH_2F}/\mathbf{CH_2}\mathrm{CF_2}$	2.20	0.24	−0.14	−0.81	2.78	4.26
	$^{\bullet}\mathrm{CHF_2}/\mathbf{CH_2}\mathrm{CF_2}$	1.94	−0.71	−0.02	−0.97	3.36	3.61
	$^{\bullet}\mathrm{CF_3}/\mathbf{CH_2}\mathrm{CF_2}$	1.56	−2.24	−0.30	−2.51	5.07	1.58
E	$^{\bullet}\mathrm{CH_3}/\mathbf{CF_2}\mathrm{CH_2}$	5.97	−0.92	−0.49	−2.94	5.97	7.59
	$^{\bullet}\mathrm{CH_2F}/\mathbf{CF_2}\mathrm{CH_2}$	4.73	−0.98	−0.15	−1.25	3.62	5.97
	$^{\bullet}\mathrm{CHF_2}/\mathbf{CF_2}\mathrm{CH_2}$	4.13	−0.81	−0.01	−1.10	2.91	5.12
	$^{\bullet}\mathrm{CF_3}/\mathbf{CF_2}\mathrm{CH_2}$	3.90	−1.21	−0.33	−2.70	5.02	4.69
F	$^{\bullet}\mathrm{CH_3}/cis\text{-}\mathrm{C_2H_2F_2}$	3.58	0.27	−0.31	−2.70	4.43	5.27
	$^{\bullet}\mathrm{CH_2F}/cis\text{-}\mathrm{C_2H_2F_2}$	2.32	0.15	−0.09	−1.19	2.25	3.44
	$^{\bullet}\mathrm{CHF_2}/cis\text{-}\mathrm{C_2H_2F_2}$	2.23	−0.74	−0.08	−1.21	2.75	2.95
	$^{\bullet}\mathrm{CF_3}/cis\text{-}\mathrm{C_2H_2F_2}$	2.04	−1.85	−0.44	−2.99	5.65	2.41
G	$^{\bullet}\mathrm{CH_3}/trans\text{-}\mathrm{C_2H_2F_2}$	3.35	0.29	−0.36	−2.65	4.51	5.14
	$^{\bullet}\mathrm{CH_2F}/trans\text{-}\mathrm{C_2H_2F_2}$	2.42	−0.15	−0.11	−1.16	3.05	4.05
	$^{\bullet}\mathrm{CHF_2}/trans\text{-}\mathrm{C_2H_2F_2}$	2.15	−0.94	−0.01	−1.15	3.23	3.29
	$^{\bullet}\mathrm{CF_3}/trans\text{-}\mathrm{C_2H_2F_2}$	1.97	−1.65	−0.28	−2.86	5.29	2.46
H	$^{\bullet}\mathrm{CH_3}/\mathbf{CHF}\mathrm{CF_2}$	3.42	0.48	−0.38	−3.12	4.44	4.84
	$^{\bullet}\mathrm{CH_2F}/\mathbf{CHF}\mathrm{CF_2}$	2.39	0.46	−0.17	−1.53	2.43	3.59
	$^{\bullet}\mathrm{CHF_2}/\mathbf{CHF}\mathrm{CF_2}$	2.21	−1.38	−0.00	−1.63	3.77	2.96
	$^{\bullet}\mathrm{CF_3}/\mathbf{CHF}\mathrm{CF_2}$	2.03	−2.65	0.45	−3.71	6.02	2.23
I	$^{\bullet}\mathrm{CH_3}/\mathbf{CF_2}\mathrm{CHF}$	4.67	−0.82	−0.47	−3.32	5.46	5.52
	$^{\bullet}\mathrm{CH_2F}/\mathbf{CF_2}\mathrm{CHF}$	3.46	−1.04	−0.18	−1.64	3.29	3.89
	$^{\bullet}\mathrm{CHF_2}/\mathbf{CF_2}\mathrm{CHF}$	3.27	−1.21	−0.10	−1.66	3.47	3.76
	$^{\bullet}\mathrm{CF_3}/\mathbf{CF_2}\mathrm{CHF}$	3.01	−1.87	−0.41	−3.68	6.18	3.23
J	$^{\bullet}\mathrm{CH_3/C_2F_4}$	3.74	−0.85	−0.31	−3.33	4.78	4.02
	$^{\bullet}\mathrm{CH_2F/C_2F_4}$	2.90	−1.40	−0.56	−2.38	4.21	2.77
	$^{\bullet}\mathrm{CHF_2/C_2F_4}$	2.71	−2.19	−0.17	−2.01	4.39	2.73
	$^{\bullet}\mathrm{CF_3/C_2F_4}$	2.38	−2.61	−0.44	−4.41	7.34	2.27

[a] All values are in kcal/mol.

radicals. Hardness parameters (η^{X}) indicated that radicals were harder than ethylenes, which is due to soft π-electrons in ethylenes.

The charge sensitivity parameters of ethylenes and radicals in the transition state geometries are shown in Table 2. Here, the charge sensitivity parameters were calculated for the reactants interacting via Mulliken point charges.[50] We applied SCCCMS to transition-state structures with neutral reactants (dissociation limit) and with charged reactants in order to obtain the energies of polarized subsystems. The values of μ_X^{M} and η_{XY}^{M} (X or Y = A or B) in Table 2 were obtained by least-squares fitting to eq 5 (see the footnote of Table 2). The trend in the chemical potentials of the reactants remained unchanged even after the interactions between the reactants were turned on. The chemical potentials of ethylenes (μ_B^{M}) were still higher than those of radicals (μ_A^{M}), which indicates that electrons flow from ethylenes into radicals in the transition states.

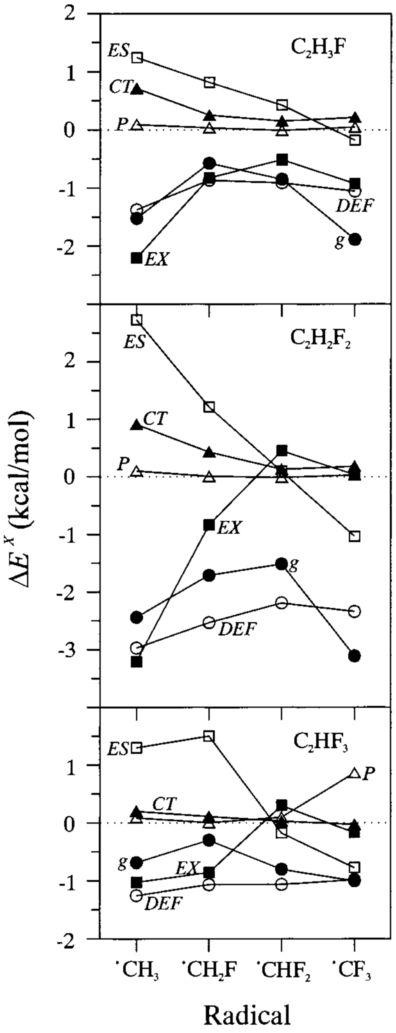

Figure 2. Energy differences between transition states with the opposite orientation of a given radical toward the double bond in unsymmetrical ethylenes (entries B vs C, D vs E, and H vs I in Table 3). The plots show excess in activation energies E^{g} as well as in each component of activation energy (ΔE^{X}; $E^{X}_{\text{less substituted}} - E^{X}_{\text{more substituted}}$; X = g, DEF, ES, CT, P, and EX).

3.2. Energy Partitioning in the Transition-State Geometries. Table 3 shows the results of energy partitioning in the transition states for the reactions in eq 1. The signs of energy terms indicate stabilizing (negative signs) or destabilizing (positive signs) contributions. Energetic requirements for each energy component are obvious from their definitions. Namely, DEF and EX terms should be positive, while P and CT contributions should be negative. The electrostatic component can be either positive or negative. The data reported in the table fulfilled these energetic requirements except for only one case. In the $^{\bullet}\mathrm{CF_3}/\mathbf{CHF}\mathrm{CF_2}$ system (hereafter, the bold face letters indicate the reaction sites for the radical addition to unsymmetrical ethylenes), the calculated P component was slightly positive.

Each term of energy partitioning was rather sensitive to the number of fluorine atoms in the attacking radical. Regardless of fluoro-substitution patterns in ethylenes, the activation energy E^{g} decreases with increase of number of fluorine atoms in the attacking radical (see the last column in Table 3). DEF and ES terms showed a trend consistent with the change in the activation energies. With an increase in the number of fluorine atoms in the attacking radical, destabilizing contribution due to the DEF term decreases and the ES contribution varies from destabilizing to stabilizing. Meanwhile, the behavior of P and CT terms were quite different. These two components are tend to be more stabilizing for the addition of $^{\bullet}CH_3$ and $^{\bullet}CF_3$ radicals than for that of $^{\bullet}CH_2F$ and $^{\bullet}CHF_2$ radicals. The EX term showed the opposite trend. Addition of $^{\bullet}CH_3$ and $^{\bullet}CF_3$ radicals results in a larger destabilizing EX contribution than that of $^{\bullet}CH_2F$ or $^{\bullet}CHF_2$ radical.

3.3. Trends in Regiochemistry of Radical Addition. The chemical potentials and hardnesses of ethylenes and radicals were sensitive to the regiochemistry of radical addition as well. As compared with addition to the more substituted site, radical addition to the less substituted site resulted in slightly higher chemical potentials (μ_B^M and μ_A^M) and slightly harder character (η_{BB}^M and η_{AA}^M) of both ethylenes and radicals (entry B vs C, D vs E, and H vs I in Table 2). The off-diagonal hardnesses (η_{AB}^M) showed the opposite behavior.

The orientation of radical addition was also reflected on each term of energy partitioning in the transition states. As seen in Figure 2, DEF components strongly facilitate addition to less fluorinated sites. The same trend can be seen for the EX component. However, EX terms slightly favor addition to more fluorinated sites for highly fluorinated systems, such as $^{\bullet}CHF_2/C_2H_2F_2$, $^{\bullet}CF_3/C_2H_2F_2$, and $^{\bullet}CHF_2/C_2HF_3$ systems. The ES components go from positive to negative values with increasing number of fluorine atoms in the radical. In the case of $^{\bullet}CH_3$ radical, ES components strongly favor addition to more fluorinated carbon atoms. This tendency is weakened with increasing number of fluorine atoms in the radical, and finally the preference is reversed. Namely, ES components show a slight preference of $^{\bullet}CF_3$ radical toward addition to less fluorinated sites. CT terms slightly favor addition to more fluorinated sites. However, the excess CT stabilization connected with orientation is less significant, as compared with DEF, EX, and ES terms. P contributions toward the regiochemistry of radical addition are still smaller and almost negligible.[53]

4. Discussion

4.1. Steric and Polar Effects. The terms “steric effect” and “polar effect” are frequently used in discussions on the mechanism of radical addition reactions. Energy partitioning enables us to quantitatively discuss the magnitude of intuitive effects, such as steric and polar effects. The magnitude of these effects can be estimated using each term of energy partitioning in our scheme. Namely, the sum of EX and DEF contributions and the sum of P, CT, and ES contributions would correspond to steric and polar effects, respectively.

Lefour et al.[20] identified the EX term as the steric effect. However, such defined “steric effect” only partially covers what experimentalists have attributed to steric repulsions.[1−3] DEF component represents destabilization due to deformation of geometry. Thus, the effects of bond weakening, rehybridization, and resonance destabilization are naturally built in DEF terms. These phenomena have been considered by Tedder as a manifestation of steric interactions.[2]

As was defined by Lefour et al.,[20] the polar effect can be identified as the sum of P, CT, and ES contributions. This definition differs from that of Pross and co-workers.[31−33] Pross et al. limited polar effect only to the CT component.[54] However, we consider that the concept of the polar effect covers not only CT contribution, but also P and ES terms. CT and ES components are both closely related to the *hard-and-soft-acids-and-bases* (HSAB) principle, which was originally introduced by Pearson.[55,56] Strong affinity of soft acid toward soft base can be interpreted as interaction controlled by CT contribution.[57] Meanwhile, ES contribution rationalizes interaction between hard acid and hard base.[58]

TABLE 4: Estimated Steric (DEF + EX) and Polar (ES + CT + P) Effects for the Reactions in Eq 1 Together with Distance (*d*) between Radical Carbon Atom and Attacked Carbon Atom of Alkene in the Transition-State Structures[a]

entry	system	steric effect	polar effect	*d*
A	$^{\bullet}CH_3/C_2H_4$	4.62	−0.22	2.389
	$^{\bullet}CH_2F/C_2H_4$	2.78	0.26	2.385
	$^{\bullet}CHF_2/C_2H_4$	2.68	−0.15	2.394
	$^{\bullet}CF_3/C_2H_4$	2.71	−1.72	2.459
B	$^{\bullet}CH_3/\mathbf{CH_2}CHF$	4.97	−0.34	2.382
	$^{\bullet}CH_2F/\mathbf{CH_2}CHF$	3.54	0.29	2.370
	$^{\bullet}CHF_2/\mathbf{CH_2}CHF$	3.47	−0.62	2.395
	$^{\bullet}CF_3/\mathbf{CH_2}CHF$	4.54	−3.42	2.449
C	$^{\bullet}CH_3/\mathbf{CHF}CH_2$	8.55	−2.40	2.311
	$^{\bullet}CH_2F/\mathbf{CHF}CH_2$	5.22	−0.83	2.298
	$^{\bullet}CHF_2/\mathbf{CHF}CH_2$	4.89	−1.19	2.308
	$^{\bullet}CF_3/\mathbf{CHF}CH_2$	6.51	−3.51	2.338
D	$^{\bullet}CH_3/\mathbf{CH_2}CF_2$	5.76	−0.60	2.359
	$^{\bullet}CH_2F/\mathbf{CH_2}CF_2$	4.98	−0.72	2.336
	$^{\bullet}CHF_2/\mathbf{CH_2}CF_2$	5.30	−1.69	2.348
	$^{\bullet}CF_3/\mathbf{CH_2}CF_2$	6.63	−5.05	2.405
E	$^{\bullet}CH_3/\mathbf{CF_2}CH_2$	11.94	−4.35	2.286
	$^{\bullet}CH_2F/\mathbf{CF_2}CH_2$	8.35	−2.38	2.266
	$^{\bullet}CHF_2/\mathbf{CF_2}CH_2$	7.03	−1.92	2.270
	$^{\bullet}CF_3/\mathbf{CF_2}CH_2$	8.93	−4.24	2.282
F	$^{\bullet}CH_3/cis\text{-}C_2H_2F_2$	8.01	−2.74	2.346
	$^{\bullet}CH_2F/cis\text{-}C_2H_2F_2$	4.75	−1.13	2.336
	$^{\bullet}CHF_2/cis\text{-}C_2H_2F_2$	4.98	−2.03	2.345
	$^{\bullet}CF_3/cis\text{-}C_2H_2F_2$	7.69	−5.28	2.375
G	$^{\bullet}CH_3/trans\text{-}C_2H_2F_2$	7.86	−2.72	2.353
	$^{\bullet}CH_2F/trans\text{-}C_2H_2F_2$	5.47	−1.42	2.336
	$^{\bullet}CHF_2/trans\text{-}C_2H_2F_2$	5.38	−2.09	2.351
	$^{\bullet}CF_3/trans\text{-}C_2H_2F_2$	7.26	−4.80	2.385
H	$^{\bullet}CH_3/\mathbf{CHF}CF_2$	7.86	−3.02	2.367
	$^{\bullet}CH_2F/\mathbf{CHF}CF_2$	4.83	−1.24	2.348
	$^{\bullet}CHF_2/\mathbf{CHF}CF_2$	5.97	−3.01	2.358
	$^{\bullet}CF_3/\mathbf{CHF}CF_2$	8.05	−5.90	2.391
I	$^{\bullet}CH_3/\mathbf{CF_2}CHF$	10.13	−4.61	2.368
	$^{\bullet}CH_2F/\mathbf{CF_2}CHF$	6.75	−2.86	2.341
	$^{\bullet}CHF_2/\mathbf{CF_2}CHF$	6.73	−2.97	2.342
	$^{\bullet}CF_3/\mathbf{CF_2}CHF$	9.20	−5.96	2.360
J	$^{\bullet}CH_3/C_2F_4$	8.51	−4.49	2.422
	$^{\bullet}CH_2F/C_2F_4$	7.11	−4.34	2.406
	$^{\bullet}CHF_2/C_2F_4$	7.10	−4.37	2.409
	$^{\bullet}CF_3/C_2F_4$	9.72	−7.46	2.433

[a] Energies and distances are given in kcal/mol and Å, respectively.

According to our definitions, we calculated the steric and polar contributions for the transition states for the reactions in eq 1. The obtained results are reported in Table 4. Noteworthy is the correlation between polar contributions and inter-reactant separations in the transition states (distance of new forming C−C bond; see the last column in Table 4). The transition states with larger separations between the reactants tend to undergo larger stabilizing polar contribution. For instance, let us consider the transition states for radical addition to the CH_2 end of monofluoroethylene. The distance of forming C−C bond alters from 2.370 to 2.449 Å in the following order: $^{\bullet}CH_2F < {}^{\bullet}CH_3 < {}^{\bullet}CHF_2 < {}^{\bullet}CF_3$. Correspondingly, the polar contribution varies from destabilizing to stabilizing (see entry B in Table 4).

4.2. Factors Responsible for Regioselectivity. In Figure 3, the differences in the steric and polar contributions between transition states for radical addition to unsymmetrical ethylenes are drawn (entry B vs C, D vs E, and H vs I in Table 4).[59] As

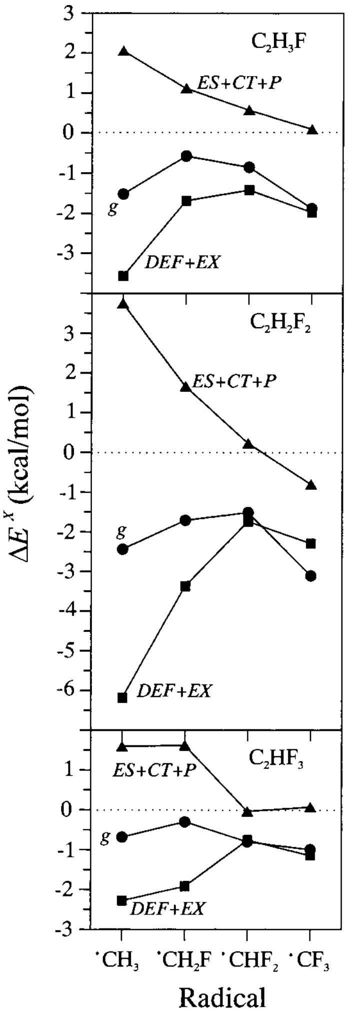

Figure 3. Same as in Figure 2 but for E^g and its resolution into polar (ES + P + CT) and steric (DEF + EX) effects.

seen in Figure 2, DEF and EX terms show a tendency to promote addition to less fluorinated sites. Consequently, the steric effect favors addition to less fluorinated sites of ethylenes, regardless of the fluoro-substitution patterns in the attacking radicals. Meanwhile, the plots of the polar contribution closely resemble those of ES terms, since the contributions of CT and P terms toward the orientation in radical addition are much less significant as compared with that of ES terms. The influence of polar effect on the regioselectivity in radical addition varies continuously with the number of fluorine atoms in the radicals. Namely, polar effect favors addition to more fluorinated sites for $^{\bullet}CH_3$ radical, while for $^{\bullet}CF_3$ radical it promotes addition to less fluorinated sites.

The steric and polar effects tend to contribute competitively toward the orientation of radical addition. These effects are highly competitive for addition of $^{\bullet}CH_3$ radical. This tendency is weakened with increasing number of fluorine atoms in the radical. Finally, for addition of $^{\bullet}CF_3$ radical, both steric and polar effects act in the same direction, i.e., facilitate addition to less substituted sites of ethylenes.

The calculated activation energies were lower for addition to less fluorinated sites than for that to more substituted sites. These results are consistent with experimental observations that free radicals should preferentially attack the less substituted carbon atom of the double bond. This preference in regiochemistry can be interpreted as steric-controlled processes since, as shown in Figure 3, the steric effect has a larger contribution toward the orientation. As Tedder pointed out previously,[2] the regioselectivity in radical addition should be mainly controlled by steric compression associated with formation of the new bond.

In contrast to general observations, $^{\bullet}CH_3$ or $^{\bullet}CH_2F$ radical preferentially attacks the CF_2 end of trifluoroethylene. Figure 3 shows that excess contributions of steric and polar effects are opposite to each other for these systems. Thus, this anomaly in regioselectivity is understandable as a polar effect dominating process. Since the ES term is a major component of the polar contribution, the reverse in regioselectivity in addition of $^{\bullet}CH_3$ or $^{\bullet}CH_2F$ radical to trifluoroethylene is attributed to electrostatic interactions.

5. Conclusions

We have investigated the mechanism of addition reactions of methyl and fluoromethyl radicals to ethylene and fluoroethylenes. The charge sensitivity analysis was carried out for the isolated reactants and the transition-state structures. In addition, to clarify predominant interactions in the transition states, our new scheme of energy partitioning was employed. The electronic activation energies were decomposed into deformation, electrostatic, polarization, charge-transfer, and exchange components.

The chemical potentials indicate that regardless of fluoro-substitution patterns in the reactants, ethylenes and radicals act as bases and acids, respectively. Namely, the electrons flow from ethylenes into radicals in all transition states. Each component of energy partitioning, as well as charge sensitivity parameters, is sensitive to the orientation of radical addition.

Our scheme of energy partitioning enables us to discuss quantitatively intuitive concepts, such as steric and polar effects. The sum of deformation and exchange energy components would correspond to the steric effect, while the polar effect can be identified as the sum of polarization, charge-transfer, and electrostatic components. The transition states with larger separations between the reactants tend to undergo larger stabilizing polar contributions. The steric effect is favorable for addition to less fluorinated sites. On the other side, the polar contribution is favorable for addition to more fluorinated sites for methyl radical. This tendency is weakened with increasing number of fluorine atoms in the radical. Finally, for trifluoromethyl radical the polar contribution favors addition to less fluorinated sites. The general observation that addition of free radicals to the double bond preferentially occurs at the less substituted site can be interpreted as a steric-controlled process. Meanwhile, the anomaly in the regioselectivity observed for addition of methyl and fluoromethyl radicals to trifluoroethylene is understandable as processes where polar effect, more specifically electrostatic effect, is dominating.

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(54) The CT term reflects the topology of the energy surface $E_M = E_M(N_A, N_B)$ and shows how charge-transfer configurations A^-B^+ and A^+B^- are coupled to the ground state (see eq 5).

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