

## Theoretical Study of Regioselectivity in Methyl Radical Additions to Fluoroethenes

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*Ab initio* calculations on the addition of methyl radicals to fluoroethene, 1,1-difluoroethene, and trifluoroethene suggest that the observed regioselectivity is the result of a delicate balance between the greater stabilization energy associated with the formation of a C-C bond when the attacked carbon is the most fluorinated one and the larger deformation energy required for this mode of attack.

Free radicals add preferentially to the less substituted carbon atom of unsymmetrical alkenes. Thus, *e.g.*, the methyl radical attacks preferentially the CH<sub>2</sub> end of fluoroethene and 1,1-difluoroethene.<sup>1</sup> In contrast, the same radical adds preferentially to the CF<sub>2</sub> end of trifluoroethene.<sup>1</sup> The origin of this reversal in the regioselectivity is the subject of numerous discussions;<sup>2,3</sup> however, no entirely satisfactory explanation has been given to date. Tedder<sup>4</sup> and more recently Giese<sup>5</sup> have proposed some rules to rationalize the reactivity and regioselectivity of free radical addition to substituted olefins. These rules indicate that the regioselectivity is mainly governed by a complex interplay of polar, steric, and bond strength

terms. The major limitation in applying these rules arises from the difficulty in evaluating the relative importance of these effects. Quantum mechanical calculations can in principle provide one solution to this problem.

We here present the results (details to be reported later) of a theoretical study of the addition reactions of the methyl radical to fluoroethene, 1,1-difluoroethene, and trifluoroethene. All calculations were carried out within the framework of *ab initio* SCF MO theory with the split-valence 4-31G basis set,<sup>6</sup> employing a locally modified version of the GAUSSIAN 80 system of programs.<sup>7</sup> The unrestricted Hartree-Fock method was used for open-shell systems.

**Table 1.** Calculated (observed) properties for the addition of methyl radicals to fluoroethenes.

Property	CH <sub>2</sub> =CH <sub>2</sub>	CH <sub>2</sub> =CHF		CH <sub>2</sub> =CF <sub>2</sub>		CHF=CF <sub>2</sub>	
		on C-1	on C-2	on C-1	on C-2	on C-1	on C-2
$\Delta E^\ddagger/(\text{kJ mol}^{-1})^a$	36.4	37.7	41.8	38.1	41.0	29.7	28.9
$E_{\text{def}}^\ddagger/(\text{kJ mol}^{-1})^b$	6.7	6.3	6.3	5.0	4.6	3.3	3.3
$E_{\text{def}}^\ddagger/(\text{kJ mol}^{-1})^c$	26.8	29.3	37.7	38.1	52.7	46.0	49.4
$E_{\text{int}}/(\text{kJ mol}^{-1})^d$	2.9	2.1	-2.1	-5.0	-16.3	-19.7	-23.8
$\Delta ZPE/(\text{kJ mol}^{-1})^e$	7.5	6.7	5.9	5.4	3.8	3.8	2.9
$\Delta S^\ddagger/(\text{J mol}^{-1} \text{K}^{-1})^f$	-119.2	-128.4	-131.8	-117.6	-123.4	-118.8	-122.6
$\Delta E_r/(\text{kJ mol}^{-1})^g$	-95.0	-100.0	-109.6	-126.4	-148.1	-165.7	-181.2
$k_1/k_2^h$		3.42 (5.0)		2.51		0.88 (0.52)	
$R/\text{\AA}^i$	2.233	2.234	2.219	2.290	2.273	2.355	2.346
$r/\text{\AA}$	1.382	1.368	1.371	1.362	1.366	1.368	1.367
$\alpha/^\circ$	108.6	108.9	108.4	108.3	108.2	106.3	108.1
$\phi/^\circ$	158.8	156.7	151.7	156.6	152.8	151.9	151.7
$\delta/^\circ$	146.7	147.3	147.8	149.9	151.1	153.7	154.0

<sup>a</sup> Potential barrier height (difference between the transition structure and reactants energies). <sup>b</sup> Methyl radical deformation energy. <sup>c</sup> Alkene deformation energy. <sup>d</sup> Interaction energy. <sup>e</sup> Zero-point vibrational energy correction. <sup>f</sup> Activation entropy at 25 °C (standard state of 1 atm). <sup>g</sup> Energy of reaction (difference between the product and reactants energies). <sup>h</sup> Orientation ratios at 164 °C. Experimental values from ref. 2. <sup>i</sup> See Figure 1 for the labelling of the geometrical parameters in the transition structure.

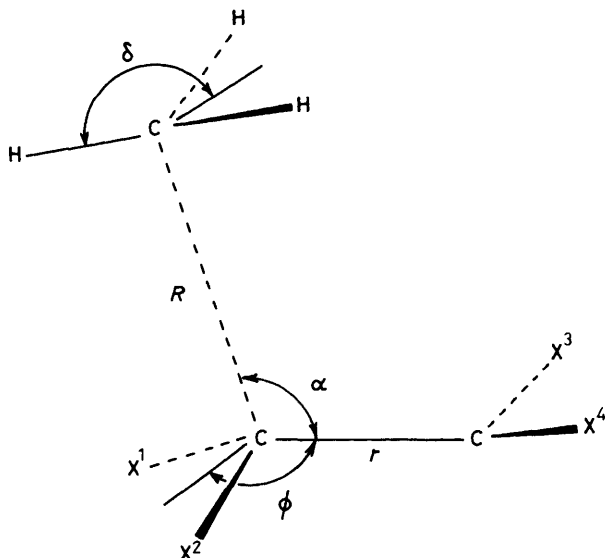


Figure 1. Labelling of geometrical parameters in Table 1.

Equilibrium geometries and transition structures were fully optimized without particular symmetry constraints by an analytical gradient procedure.<sup>8</sup> The harmonic vibrational frequencies of both reactants and transition structures were determined by diagonalizing the matrix of the mass-weighted cartesian force constants obtained by finite differences of analytical gradients. The zero-point vibrational energies and entropy changes were evaluated from the calculated frequencies multiplied by a scaling factor (0.89) to correct for electron correlation and vibrational anharmonicity effects.<sup>9</sup>

The calculated potential barrier heights, zero-point vibrational energy corrections, activation entropies at 25 °C, energies of reaction, and orientation ratios at 164 °C are shown in Table 1, together with the most relevant geometrical parameters of the transition structures. For comparison purposes, the results of our recent study<sup>9</sup> of methyl radical addition to ethene are also given. For a deeper understanding and chemical interpretation of the regioselectivity, the potential barrier heights are partitioned into a sum of three contributions: the molecular deformation energy of the radical ( $E_{\text{def}}^{\text{R}}$ ) and the alkene ( $E_{\text{def}}^{\text{A}}$ ), and the interaction energy ( $E_{\text{int.}}$ ). A further dissection of the latter term, according to the Morokuma scheme,<sup>10</sup> will be reported in the full paper.

Our calculations correctly predict the preferred mode of attack to fluoroethene and 1,1-difluoroethene to be at the less substituted carbon atom (C-1). Methyl radical addition to trifluoroethene is predicted to take place most readily at the most substituted end of the alkene (*i.e.* C-2), in agreement with experiment. The calculated orientation ratios at 164 °C for addition to fluoroethene (3.42) and trifluoroethene (0.88) are in fairly good agreement with the experimental ratios (5.0 and 0.52, respectively).<sup>2</sup> The entropy term always favours addition to C-1 and its contribution to the regioselectivity is not negligible but is nearly compensated by the opposite trend of zero-point corrections. It is also noteworthy that the observed relative overall rate of addition of methyl radicals to fluoroethenes (*e.g.*,  $\text{CHF}=\text{CF}_2 > \text{CH}_2=\text{CH}_2 > \text{CH}_2=\text{CHF} > \text{CH}_2=\text{CF}_2$ ) is correctly reproduced by the present calculations.

The reversal of the regioselectivity in the addition of methyl radicals to trifluoroethene can be rationalized in terms of the calculated energies of reaction ( $\Delta E_r$ ) and the component analysis of the potential barrier heights. First, we note that the attack to the more substituted end of the fluoroethenes

studied is always the more exothermic pathway; the largest difference in  $\Delta E_r$  between the two modes of attack is found for the addition to 1,1-difluoroethene. It is, therefore, noteworthy that the preferred mode of attack to both fluoroethene and 1,1-difluoroethene is contrathermodynamic since the potential barrier of the more exothermic pathway is the larger one. Next, we note that the higher barrier for the attack to the most substituted site of the two latter fluoroethenes is essentially due to the larger deformation energy of the alkene for this mode of attack. This feature can be related mainly to the larger pyramidalization of the attacked centre in the transition structure, as measured by the geometrical parameter  $\phi$  in Figure 1. In the case of the addition to trifluoroethene, although the deformation energy of the alkene still is larger for attack at the  $\text{CF}_2$  end, the difference between the  $E_{\text{def.}}^{\text{A}}$  terms for the two modes of attack is substantially reduced. Notice that this result again is consistent with nearly the same pyramidalization calculated for the attacked centre in both transition structures. Finally, we note that as the number of fluorine atoms in the carbon atom undergoing attack increases, the  $E_{\text{int.}}$  contribution to the barrier height becomes more stabilizing. This effect can be related to the greater bond energy of the newly formed C-C bond in the corresponding adduct radical, judged by the calculated energies of reaction. The point to be noted here is that if one compares the two modes of addition to an unsymmetrical fluoroethene, the  $E_{\text{def.}}^{\text{A}}$  and  $E_{\text{int.}}$  contributions to the barrier height change in opposite sense. Thus, in passing from the attack at the less substituted site to the most substituted one, the  $E_{\text{def.}}^{\text{A}}$  term increases the barrier height while the  $E_{\text{int.}}$  term decreases it. The net result is a clear dominance of the role played by the increase in the  $E_{\text{def.}}^{\text{A}}$  term, except in the case of trifluoroethene where, as mentioned above, this term suffers a relatively small increase that is outweighed by the increased stabilization due to the  $E_{\text{int.}}$  contribution.

In summary, we conclude that the observed regioselectivity in the addition of methyl radicals to unsymmetrical fluoroethenes is the result of a delicate balance between the greater stabilization energy that accompanies the formation of the incipient C-C bond when the attacked carbon atom is the most fluorinated one and the larger deformation energy of the alkene which is required for this mode of attack.

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