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Density Functional Study of Addition of Fluoromethyl Radicals to Fluoroethylenes: Estimation of Activation Energies

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The addition reactions of $^{\bullet}CH_3$, $^{\bullet}CH_2F$, $^{\bullet}CHF_2$, and $^{\bullet}CF_3$ radicals to ethylene, monofluoroethylene, difluoroethylene, trifluoroethylene, and tetrafluoroethylene have been investigated using density functional theory (DFT, Kohn−Sham scheme) and Hartree−Fock (HF) methods. In the DFT calculations, we have used both pure and hybrid (partly including HF) exchange and Lee/Yang/Parr or Perdew/Wang 91 correlation functionals with the 6-31G* basis set. The same basis was taken in the HF calculations. For all possible combinations of fluorosubstituted methyl radicals and ethylenes, structures of reactants and transition states have been located. Inclusion of electron correlation was shown to be important in reproducing experimental activation barriers, though the results were strongly dependent on the type of functionals. The Becke's three-parameter hybrid with Perdew/Wang 91 gradient-corrected correlation functional B3PW91 gave the best estimates of the activation energies.

Introduction

The reactions of radical addition to substituted alkenes are well documented experimentally[1−3] due to their importance in synthesis of organic compounds, including industrial applications in polymer technology. Thus, many experimental works have been carried out to understand the influence of substituents in alkenes and in radicals on regio- and stereoselectivity.[4−6] The role of various physical effects (e.g., polarization of the transition states, relative strength of the bonds being broken and formed, steric hindrance, and resonance stabilization) was analyzed,[4−6] leading to intuitive chemical rules[5,6] which rationalized the observed selectivities.

In this paper, we report theoretical investigations on the addition reactions of the fluoromethyl radicals to fluoroethylenes,

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

where $n = 0$, 1, 2, or 3 and $m = 0$, 1, 2, 3, or 4, respectively. All possible reactive systems starting from methyl radical and ethylene up to trifluoromethyl radical and tetrafluoroethylene were taken into consideration. We have concentrated our efforts on accurate evaluation of the activation barriers. We used methods based on density functional theory (DFT).[7] This choice is in conjunction with recent successful applications of DFT to various radical systems.[8−12] In addition, Hartree−Fock (HF) method was applied as a reference which does not include electron correlation.

Several theoretical studies related to reaction 1 are available. The results concerning such systems as $^{\bullet}CH_3/C_2H_4$,[11−23] $^{\bullet}CH_2F/C_2H_4$,[12] $^{\bullet}CF_3/C_2H_4$,[12,23] $^{\bullet}CH_3/C_2H_3F$,[13−16,20] $^{\bullet}CH_3/C_2H_2F_2$,[15,20] $^{\bullet}CH_3/C_2HF_3$,[15,16] $^{\bullet}CF_3/C_2H_3F$,[16] and $^{\bullet}CF_3/C_2HF_3$[16] have been reported. Bottoni[12] has reached the conclusion that inclusion of dynamic correlation is essential for reasonable values of computed activation energies. DFT method using hybrid B3LYP functional and MP2 calculations have been shown to provide reasonable activation barrier heights in most cases. In some cases, still higher computational levels, such as MP4,[12] QCISD, and QCISD(T),[13,14] were needed for accurate estimation of activation energies.

It has been generally accepted that the reactivity in the systems of fluoro-substituted alkenes and radicals can be rationalized with the polar effects. However, it is still questionable to what extent the polar effects are predominant in governing the reactivity in these systems. Recent theoretical studies by Wong et al.[13,14] suggested that polar contributions to the reactivity in radical addition to alkenes are insignificant. To examine generality of their conclusion, it is essential to find an "inexpensive" computational model that can be applied to various systems, including the reactants containing large substituents. We describe here that the hybrid DFT method using combination of Becke's three-parameter functional and Perdew/Wang 91 correlation functional (B3PW91) provides reasonable activation barrier heights for addition of fluoromethyl radicals to fluoroethylenes.

Methods

All calculations were carried out using Gaussian 94/DFT suite of programs[24] on an IBM 6000. The 6-31G* basis set[25] was adopted. We have located transition states on the minimum-energy-paths, as well as the minimum energy structures of the reactants. Geometrical degrees of freedom were fully optimized. The nature of the stationary points was assessed by vibrational frequency analysis. In the DFT calculations, we used two pure and two hybrid functionals. The combinations of the Becke's 1988 exchange functional[26] and the correlation functional of Lee/Yang/Parr[27,28] or Perdew/Wang 91 gradient-corrected correlation functional[29] were used for pure DFT calculations. Throughout the paper, these combinations will be denoted as

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TABLE 1: Activation Energies (kcal/mol) Predicted at Hartree−Fock (Column A) and Density Functional [Columns B (BLYP), B′ (B3LYP), C (BPW91), and C′ (B3PW91)] Levels of Theory

		model I[b]					model II[c]					
entry	system[a]	A	B	B′	C	C′	A	B	B′	C	C′	exptl[d]
a	$^\bullet\mathrm{CH_3/C_2H_4}$	11.6	5.3	6.7	5.5	6.6	11.7	5.8	7.1	6.0	7.1	7.7
	$^\bullet\mathrm{CH_2F/C_2H_4}$	8.6	4.1	5.3	4.2	5.3	9.4	5.2	6.4	5.4	6.4	4.3
	$^\bullet\mathrm{CHF_2/C_2H_4}$	6.6	2.0	3.2	2.4	3.4	7.7	3.3	4.4	2.9	4.6	
	$^\bullet\mathrm{CF_3/C_2H_4}$	4.1	−0.1	0.9	0.8	1.5	5.4	1.5	2.3	2.4	3.0	2.9
b	$^\bullet\mathrm{CH_3}/\mathbf{CH_2}\mathrm{CHF}$	12.4	5.1	6.6	5.3	6.7	12.8	5.8	7.3	6.1	7.3	8.1
	$^\bullet\mathrm{CH_2F}/\mathbf{CH_2}\mathrm{CHF}$	9.7	4.1	5.6	4.4	5.6	10.8	5.5	6.8	5.7	6.9	
	$^\bullet\mathrm{CHF_2}/\mathbf{CH_2}\mathrm{CHF}$	7.6	1.9	3.2	2.4	3.4	9.1	3.4	4.6	3.9	4.9	
	$^\bullet\mathrm{CF_3}/\mathbf{CH_2}\mathrm{CHF}$	5.7	−0.4	0.8	0.5	1.5	7.3	1.3	2.4	2.2	3.1	3.3
c	$^\bullet\mathrm{CH_3}/\mathbf{CHF}\mathrm{CH_2}$	13.2	6.7	8.0	7.1	8.2	13.6	7.2	8.5	7.7	8.7	8.4
	$^\bullet\mathrm{CH_2F}/\mathbf{CHF}\mathrm{CH_2}$	9.9	5.0	6.2	5.4	6.4	10.9	6.2	7.4	6.7	7.6	
	$^\bullet\mathrm{CHF_2}/\mathbf{CHF}\mathrm{CH_2}$	8.1	2.7	3.7	3.2	4.1	9.5	4.1	5.2	4.7	5.6	
	$^\bullet\mathrm{CF_3}/\mathbf{CHF}\mathrm{CH_2}$	6.8	1.3	2.4	2.3	3.1	8.4	3.0	4.0	3.9	4.7	4.8
d	$^\bullet\mathrm{CH_3}/\mathbf{CH_2}\mathrm{CF_2}$	13.6	5.2	7.1	5.5	7.1	14.3	6.1	7.8	6.4	7.9	
	$^\bullet\mathrm{CH_2F}/\mathbf{CH_2}\mathrm{CF_2}$	11.4	4.5	6.2	4.7	6.3	12.8	6.0	7.6	6.3	7.7	
	$^\bullet\mathrm{CHF_2}/\mathbf{CH_2}\mathrm{CF_2}$	10.2	2.2	3.8	2.7	4.1	11.9	3.8	5.4	4.4	5.7	
	$^\bullet\mathrm{CF_3}/\mathbf{CH_2}\mathrm{CF_2}$	8.1	−0.4	1.1	0.5	1.8	9.9	1.5	2.9	2.4	3.6	4.1
e	$^\bullet\mathrm{CH_3}/\mathbf{CF_2}\mathrm{CH_2}$	14.3	7.3	8.8	8.2	9.3	15.0	8.0	9.4	8.9	10.0	9.9
	$^\bullet\mathrm{CH_2F}/\mathbf{CF_2}\mathrm{CH_2}$	11.6	5.6	7.1	6.4	7.7	14.4	7.0	8.4	7.9	9.0	
	$^\bullet\mathrm{CHF_2}/\mathbf{CF_2}\mathrm{CH_2}$	9.8	3.1	4.5	4.0	5.2	11.6	4.8	6.1	5.7	6.8	
	$^\bullet\mathrm{CF_3}/\mathbf{CF_2}\mathrm{CH_2}$	9.2	1.9	3.3	3.2	4.4	11.2	3.0	4.4	5.0	6.2	6.1
f	$^\bullet\mathrm{CH_3}/cis\mathrm{-C_2F_2H_2}$	12.1	5.3	6.8	5.9	7.1	12.7	6.1	7.5	6.7	7.8	
	$^\bullet\mathrm{CH_2F}/cis\mathrm{-C_2F_2H_2}$	8.8	3.6	4.9	4.2	5.3	10.1	5.1	6.4	5.7	6.7	
	$^\bullet\mathrm{CHF_2}/cis\mathrm{-C_2F_2H_2}$	7.4	1.5	2.7	2.2	3.2	9.0	3.2	4.4	3.9	4.9	
	$^\bullet\mathrm{CF_3}/cis\mathrm{-C_2F_2H_2}$	6.8	0.2	1.6	1.3	2.4	8.7	2.1	3.4	3.1	4.2	
g	$^\bullet\mathrm{CH_3}/trans\text{-}\mathrm{C_2F_2H_2}$	11.6	5.2	6.7	5.8	7.0	12.1	6.0	7.4	6.6	7.7	
	$^\bullet\mathrm{CH_2F}/trans\text{-}\mathrm{C_2F_2H_2}$	9.4	4.3	5.6	4.7	5.9	10.7	5.7	7.0	6.2	7.3	
	$^\bullet\mathrm{CHF_2}/trans\text{-}\mathrm{C_2F_2H_2}$	7.6	1.8	3.1	2.5	3.6	9.3	3.4	4.7	4.1	5.2	
	$^\bullet\mathrm{CF_3}/trans\text{-}\mathrm{C_2F_2H_2}$	6.6	0.3	1.7	1.4	2.5	8.4	2.0	3.4	3.2	4.3	
h	$^\bullet\mathrm{CH_3}/\mathbf{CHF}\mathrm{CF_2}$	10.7	4.6	6.2	5.2	6.6	11.6	5.5	7.1	6.2	7.4	
	$^\bullet\mathrm{CH_2F}/\mathbf{CHF}\mathrm{CF_2}$	8.9	3.5	5.0	4.1	5.3	10.5	5.1	6.5	5.7	6.9	
	$^\bullet\mathrm{CHF_2}/\mathbf{CHF}\mathrm{CF_2}$	7.7	1.2	2.7	2.0	3.2	9.6	3.0	4.4	3.8	4.9	
	$^\bullet\mathrm{CF_3}/\mathbf{CHF}\mathrm{CF_2}$	7.4	−0.3	1.3	0.8	2.2	9.5	1.6	3.2	2.8	4.1	4.8
i	$^\bullet\mathrm{CH_3}/\mathbf{CF_2}\mathrm{CHF}$	10.6	4.6	6.2	5.2	6.6	11.6	5.8	7.3	6.8	8.0	
	$^\bullet\mathrm{CH_2F}/\mathbf{CF_2}\mathrm{CHF}$	8.1	3.2	4.8	4.2	5.4	11.4	4.9	6.3	5.8	7.0	
	$^\bullet\mathrm{CHF_2}/\mathbf{CF_2}\mathrm{CHF}$	7.6	1.5	3.0	2.5	3.8	9.6	3.3	4.8	4.3	5.6	
	$^\bullet\mathrm{CF_3}/\mathbf{CF_2}\mathrm{CHF}$	7.3	0.1	1.8	1.5	2.9	9.5	2.1	3.8	3.5	4.9	5.5
j	$^\bullet\mathrm{CH_3/C_2F_4}$	6.1	3.0	4.7	4.1	5.5	7.6	4.2	5.7	5.3	6.5	5.9
	$^\bullet\mathrm{CH_2F/C_2F_4}$	5.0	1.8	3.5	3.0	4.3	7.1	3.6	4.7	4.7	5.9	
	$^\bullet\mathrm{CHF_2/C_2F_4}$	5.1	0.3	1.9	1.5	2.8	7.4	2.2	3.7	3.3	4.6	
	$^\bullet\mathrm{CF_3/C_2F_4}$	5.2	−1.0	0.8	0.5	2.0	7.7	1.1	2.8	2.6	4.1	4.6

[a] Bold face letters represent the attacked reaction sites in unsymmetrical alkenes. [b] Model I corresponds to energy difference between transition state and reactants (including zero-point vibrational corrections). [c] Model II corresponds to fit to the Arrhenius equation over the temperature range 300−500 K. [d] Experimental values are taken from ref 4.

BLYP and BPW91. In addition, the combinations of Becke's three-parameter functional,[30] which partly includes HF exchange, and Lee/Yang/Parr or Perdew/Wang 91 correlation functional (B3LYP and B3PW91) were used for hybrid DFT calculations. The geometries and energies of the transition states and reactants are available as supporting material.

Recently Wittbrodt and Schlegel[31] showed that spin projection can seriously distort shape and quality of potential energy surface calculated by DFT methods, just as spin projection can yield poor results for HF potential energy surfaces. Distortion of potential energy curves caused by spin projection will be considerably large for bond formation/dissociation, and sometimes leads to "negative activation energies". Thus, we did not use spin projection technique in DFT and HF calculations.

Activation energy is an experimentally derived quantity; it is defined as the slope of Arrhenius plot [ln $k(T)$ versus $1/T$], i.e.,

$$E_\mathrm{a} \equiv -R\mathrm{d}\ln k(T)/\mathrm{d}(1/T) \qquad (2)$$

where T, $k(T)$, and R are temperature, rate and gas constants, respectively. Frequently calculated energy difference $\Delta E^{\neq}$ between transition state and reactant(s) is compared with activation energy. Namely, the activation energy for reaction 1 might be approximated as follows (model I),

$$E_\mathrm{a} \approx \Delta E^{\neq} = E_0^{\mathrm{TS}} - E_0^{\mathrm{radical}} - E_0^{\mathrm{alkene}} \qquad (3)$$

Here E_0^{TS}, E_0^{radical}, E_0^{alkene} are the energies (including zero-point vibrational corrections) of the transition state, radical, and alkene, respectively. However, this definition of "activation energy at $T = 0$ K" does not include translational and all internal energy contributions. Thus, we calculated activation energies via eq 2. Energy barriers reported for the reaction 1 were derived from experimentally measured rate constants over temperature range 300−500 K. According to the conventional transition state theory,[32] we have calculated the rate constants for this temperature region. The transmission coefficient was fixed to unity. The obtained rate constants gave straight Arrhenius lines. We derived the activation energies by least-squares fitting to the Arrhenius equation [$\ln k(T) = \ln A - E_\mathrm{a}/RT$]; the correlation coefficients were higher than 0.997 (model II).

Results and Discussion

Table 1 gives activation energies calculated with models I and II along with those experimentally derived (the last column).

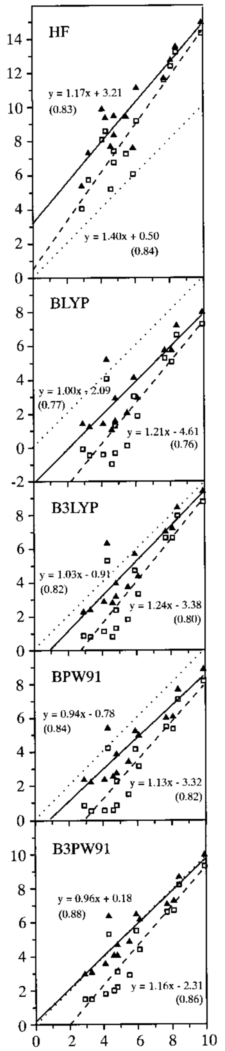

Figure 1. Correlation diagrams between experimental, (horizontal axes), and calculated (vertical axes) activation energies E_a at the UHF/6-31G* and DFT/6-31G* levels of theory. Open squares correspond to model I, while closed triangles to model II. Linear least-squares fittings ($y = ax + b$) gave broken and solid lines with the correlation coefficients in parentheses for model I and II, respectively. The dotted lines represent ideal correlation ($y = x$). The numerical values are reported in Table 1.

Figure 1 shows the correlations between calculated activation energies (vertical axes: y) and experimental values (horizontal axes: x). Linear least-squares fittings ($y = ax + b$) gave broken and solid lines for models I and II, respectively. The dotted lines represent ideal correlation ($y = x$). Regardless of computational levels utilized, the slopes of fitted lines for model II (the solid lines) were closer to the ideal value of unity than those for model I (the broken lines). From theoretical standpoint, the experimental values for the activation energies do not correspond to $\Delta E^{\ddagger}$ (model I). Thus, we hereafter discuss the values for activation energies computed using model II.

Activation energies derived from HF calculations were always larger than experimental values. Overestimation of activation energies clearly originates from significant spin contamination of the wavefunctions of the transition states. The values of $\langle S^2 \rangle$ were greater than 1.0 for the transition states, while $\langle S^2 \rangle$ did not exceed 0.762 for the reactant fluoromethyl radicals. As compared to the HF calculations, spin contamination for the transition states was much less significant in DFT cases; $\langle S^2 \rangle$ did not exceed 0.766 and 0.782 in the pure and hybrid DFT calculations, respectively. Thus, spin contamination for the transition states was almost comparable to that for the reactant radicals ($\langle S^2 \rangle \leq 0.755$).

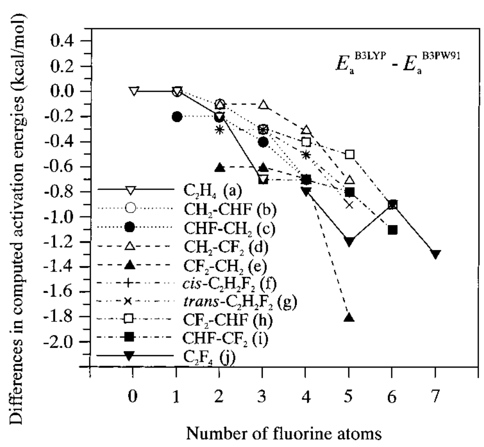

Figure 2. Differences between activation energies obtained in B3LYP and B3PW91 calculations, plotted for each entry distinguished in Table 1, as a function of the number of fluorine atoms in the systems.

The DFT calculations using pure functionals (BLYP and BPW91) showed a tendency to systematically underestimate activation energies. The computed values were lower than the experimental values, except for $^{\bullet}CH_2F/C_2H_4$ system. The deviation from the experimental values was 2.2 and 1.3 kcal/mol in average for BLYP and BPW91 activation energies, respectively. The slopes of the fitted lines, 1.00 for BLYP and 0.94 for BPW91 (Figure 1), were close to the ideal value.

The systematic underestimation of activation energies observed for the pure DFT results was reduced for the hybrid DFT calculations. The activation energies computed with the hybrid DFT methods (B3LYP and B3PW91) were always larger than those computed with the corresponding pure DFT methods. Average deviation from the experimental values was significantly reduced in the hybrid DFT calculations (1.0 and 0.5 kcal/mol for B3LYP and B3PW91 activation energies, respectively). The values of the slope of the fitted lines, 1.03 and 0.96 for B3LYP and B3PW91, were comparable to those observed for the corresponding pure DFT results (Figure 1).

Experimental results indicate that the activation energy decreases with increase of the number of fluorine atoms in the reactant radical. This trend can be seen regardless of the structure of alkenes. Moreover, activation energies for the attack on less-fluorinated carbon atom tend to be lower than that on highly fluorinated site. The DFT activation energies, as well as those calculated with HF method, qualitatively reproduced these effects of fluorine substitution.

For both pure and hybrid DFT calculations, Lee/Yang/Parr functional suggested more pronounced effect of fluorine substitution as compared to Perdew/Wang 91 functional. The difference between B3LYP and B3PW91 activation energies increased with increasing number of fluorine atoms in the systems (see Figure 2). The B3LYP and B3PW91 activation energies were nearly the same for the parent system ($^{\bullet}CH_3/C_2H_4$: 7.1 kcal/mol), as well as for monofluorinated systems ($^{\bullet}CH_2F/C_2H_4$, 6.4 kcal/mol; $^{\bullet}CH_3/CH_2CHF$, 7.3 kcal/mol); the differences between computed activation energies were smaller than 0.1 kcal/mol. In totally fluorinated $^{\bullet}CF_3/C_2F_4$ system, the B3LYP and B3PW91 activation energies were quite different: 2.8 and 4.1 kcal/mol, respectively. The corresponding pure DFT calculations (BLYP and BPW91) showed similar trend. The activation energies computed using Perdew/Wang 91 functional were closer to the experimental values, even for highly fluorinated systems, than those computed using Lee/Yang/Parr functional (see Table 1). Thus, Lee/Yang/Parr functional has a tendency to overestimate the fluorine substitution effects.

Our results indicated that B3PW91 calculations gave the best estimates of the activation energies for fluoromethyl radical addition to fluoroethylenes. Deviation from the experimental values was less than 0.8 kcal/mol with one exceptional case of $^{\bullet}CH_2F/C_2H_4$, where the deviation was the largest (2.1 kcal/mol). Linear fitting between computed (y) and experimental (x) values (in kcal/mol) gave the relationship $y = 0.96x + 0.18$ with correlation coefficient equal to 0.88. After omitting the exceptional case, the correlation coefficient increased up to 0.96.

Conclusions

In this paper we have reported the systematic HF and DFT studies of the addition reactions of $^{\bullet}CH_3$, $^{\bullet}CH_2F$, $^{\bullet}CHF_2$ and $^{\bullet}CF_3$ radicals to ethylene, monofluoroethylene, difluoroethylene, trifluoroethylene, and tetrafluoroethylene. Activation energies obtained in HF scheme are overestimated, while the pure DFT functionals (BLYP and BPW91) have a tendency to underestimate the activation energies. This tendency is significantly reduced in the hybrid (B3LYP and B3PW91) calculations. The effect of fluorine substitution on the activation energies is qualitatively reproduced in DFT approaches, as well as HF method. However, DFT method using Lee/Yang/Parr correlation functional exaggerates fluorine substitution effect. In contrast, Perdew/Wang 91 functional leads to more quantitative description of the fluorine substitution. The Becke's three-parameter hybrid with Perdew/Wang 91 gradient-corrected correlation functional (B3PW91) gives the best agreement with available activation energies.

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Supporting Information Available: Tables of the optimized geometrical parameters (Tables IS−VS) and the absolute energies of the transition states and reactants (Tables VIS and VIIS) and figures defining the geometrical parameters reported in Tables IS−VS and showing the optimized transition state structures at the B3PW91 level of theory (Figures 1S and 2S) (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Minisci, F.; Citterio, A. *Adv. Free Radical Chem.* **1980**, *6*, 65.

(2) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, Structure*; Wiley: New York, 1985.

(3) Giese, B., Baldwin, J.E., Ed.; *Radical in Organic Synthesis: Formation of the Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986.

(4) Tedder, J. M.; Walton, J. C. *Adv. Phys. Org. Chem.* **1978**, *16*, 51 and references therein.

(5) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401.

(6) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753.

(7) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(8) Barone, V. *Recent Advances in Computational Chemistry - Vol. 1 (Recent Advances in Chemistry Density Functional Methods Part 1)*; World Scientific: Singapore, 1995; p 287.

(9) Batra, R.; Giese, B.; Spichty, M. *J. Phys. Chem.* **1996**, *100*, 18371.

(10) Basch H.; Hoz, S. *J. Phys. Chem.* **1997**, *101*, 4416.

(11) Barone, V.; Orlandini, L. *Chem. Phys. Lett.* **1995**, *246*, 45.

(12) Bottoni, A. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2041.

(13) Wong, M.W.; Pross, A.; Radom, L . *J. Am. Chem. Soc.* **1993**, *115*, 11050.

(14) Wong, M.W.; Pross, A.; Radom, L . *J. Am. Chem. Soc.* **1994**, *116*, 6284.

(15) Arnaud, R.; Subra, R.; Barone, V.; Lelj, F.; Olivella, S.; Sole, A.; Russo, N. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1517.

(16) Bonacic-Koutecky, V.; Koutecky, J.; Salem, L. *J. Am. Chem. Soc.* **1977**, *99*, 842.

(17) Houk, K. N.; Paddon-Row, M. N.; Spellmeyer, D. C.; Rondan, N. G.; Nagase, S. *J. Org. Chem.* **1986**, *51*, 2874.

(18) Gonzales, C.; Sosa, C.; Schlegel, H. B. *J. Phys. Chem.* **1989**, *93*, 2435.

(19) Zipse, H.; He, J.; Houk, K. N.; Giese, B. *J. Am. Chem. Soc.* **1991**, *113*, 4324.

(20) Donovan, W. H.; Famini, G. R. *J. Phys. Chem.* **1994**, *98*, 7811.

(21) Fueno, T.; Kamachi, M. *Macromolecules* **1988**, *21*, 908.

(22) Tozer, D. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C. *Chem. Phys. Lett.* **1992**, *199*, 229.

(23) Arnaud, R. *New. J. Chem.* **1989**, *13*, 543.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94/DFT, Revision D.1; Gaussian, Inc.: Pittsburgh PA, 1995.

(25) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(26) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(27) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(28) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(29) Perdew, J. P.; Wang. Y. *Phys. Rev. B* **1992**, *45*, 13244.

(30) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(31) Wittbrodt, J. M.; Schlegel, H. B. *J. Chem. Phys.* **1996**, *105*, 6574.

(32) Pacey, P. D. *J. Chem. Educ.* **1981**, *58*, 612.