CROATICA CHEMICA ACTA CCACAA **67** (2) 189–195 (1994)

ISSN 0011-1643
CCA–2176

Original Scientific Paper

An *ab initio* Molecular Orbital Study of the Insertions of Difluorocarbene into Substituted Ethenes

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Received September 30, 1993

Ab initio MO calculations predict the activation energies for the insertions of difluorocarbene into substituted ethenes C_2H_3X (X = F, Cl, Me) to be 61,68 and 52 kJ mol^{-1}, respectively; these results indicate that the monosubstitution on the ethene has no significant effects on the activation energy of the reaction.

INTRODUCTION

The cycloadditions of singlet carbenes to ethene have been studied extensively by various theoretical methods. Recently both *ab initio*[1–3] and semi-empirical[4] MO calculations have been carried out to investigate the effects of substituents on the carbene upon the reactions. However, very little work has been done to investigate the effect when the substituents are placed on the ethene. Our previous work[3] shows that inclusion of correlation effects in *ab initio* MO calculations yields an activation energy for addition of difluorocarbene to ethene that is in excellent agreement with experimental result. Therefore, it is of interest to extend our investigation to study the effects of substituents on the ethene upon the cycloaddition reactions using correlated *ab initio* MO calculations. It is noted that insertion of difluorocarbene into ethene is one of the few simple carbene cycloadditions that require activation energy and for which comparison between experimental and calculated results can be made. Hence, in the present study, we have once again chosen fluorocarbene as the inserting agent and the substituted ethenes selected for investigation include fluoroethene, chloroethene and propene.

METHOD OF CALCULATION

Standard *ab initio* molecular orbital calculations were carried out using the Gaussian 90[5] and Gaussian 92[6] programs. Geometries of the structures were determined at the spin-restricted Hartree-Fock (RHF) level with the 6-31G** [6-31G(d,p)] basis set, as well as at the (restricted) second-order Møller-Plesset theory [RMP2(FU)] with

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the same basis set. In order to characterize the stationary points found as minima (equilibrium structures) or saddle points (transition structures) on the potential energy surface, and to include the effects of zero-point vibrational energies in estimating the relative energies of the various species, harmonic vibrational frequencies were calculated at the Hartree-Fock level with the 6-31G** basis. As such calculations are known to overestimate vibrational frequencies by *ca.* 10%,[7] the zero-point vibrational contributions were scaled down by a factor of 0.9 in the calculation of related energies. The effects of valence-electron correlation on relative energies were determined from the fourth-order Møller-Plesset perturbation theory[8] (MP4). The relative energies obtained at MP4(FC)/6-31G** level were estimated from the following additivity approximation:

$$\Delta E(\mathrm{MP4/6\text{-}31G^{**}}) \approx \Delta E(\mathrm{MP4/6\text{-}31G}) - \Delta E(\mathrm{MP2/6\text{-}31G}) + \Delta E(\mathrm{MP2/6\text{-}31G^{**}}) \quad (1)$$

This additivity scheme has previously[9] been proved to be reliable.

RESULTS AND DISCUSSION

Optimized structures of the transition states (TSs) of the three reactions under study (CF_2 + C_2H_3X, X = F, Cl, Me) are shown in Figures 1 to 3, respectively. Calculated total energies, zero-point vibration energies (ZPVE) and relative energies are summarized in Table I.

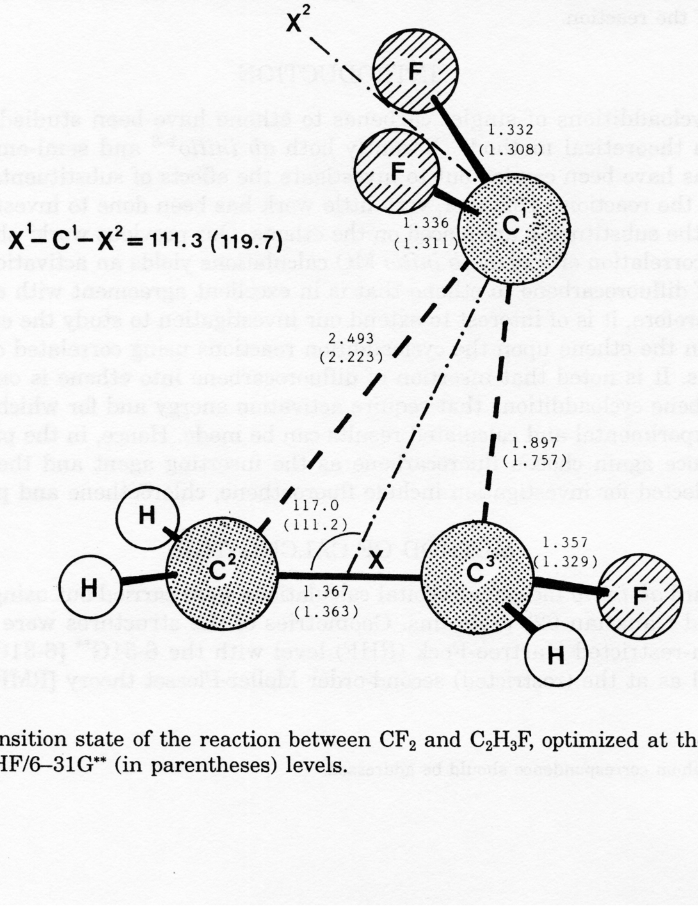

Figure 1. Transition state of the reaction between CF_2 and C_2H_3F, optimized at the MP2(FU)/6–31G** and HF/6–31G** (in parentheses) levels.

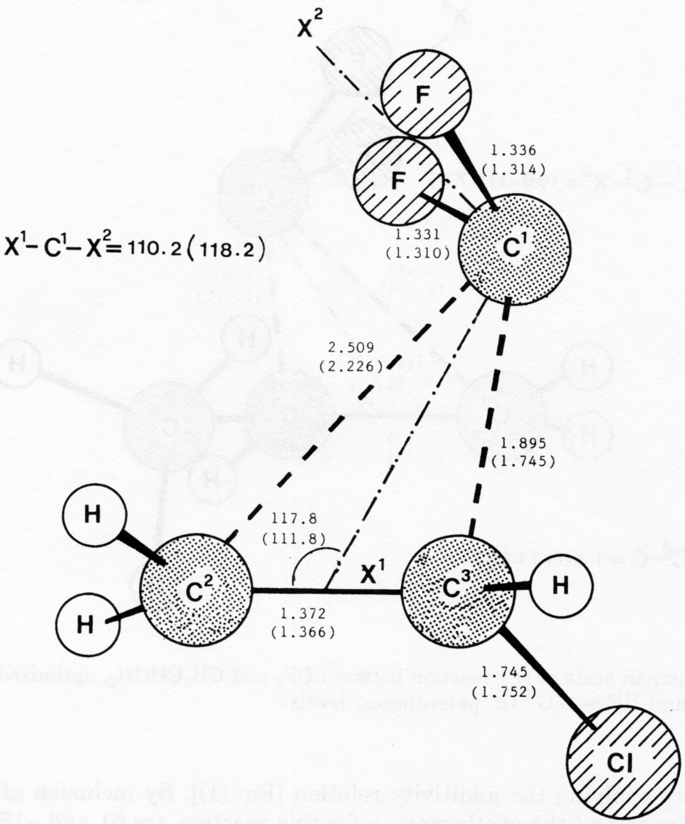

Figure 2. Transition state of the reaction between CF_2 and C_2H_3Cl, optimized at the MP2(FU)/6–31G** and HF/6–31G** (in parentheses) levels.

For the reaction between CF_2 and C_2H_3F, on examining the structures of the TS shown in Figure 1, it is seen that, at both the HF/6-31G** and MP2/6-31G** levels of theory, the TS has C_1 symmetry. Qualitatively, it is of the Hoffmann type[10] transition structures, with the methylene carbon (C^1) being closer to the carbon with the fluorine (C^3). Quantitatively, the optimized geometry at the MP2/6-31G** level is rather different from that at HF/6-31G** level of theory. The most striking feature is the change in the C^1–C^2 distance: inclusion of correlation effects lengthens the C^1–C^2 distance by about 0.3 Å. This change in geometry from HF/6-31G** to MP2/6-31G** leads to a 13 kJ mol^{-1} decrease in the activation energy calculated at the HF/6-31G** level of theory. By inclusion of correlation effects calculated at the MP2 level of theory, the barrier is reduced by 84 and 65 kJ mol^{-1} for the optimized HF/6-31G** and MP2/6-31G** structures, respectively. On the other hand, employing more sophisticated electron-correlated methods beyond the MP2 level of theory does not lead to energy changes of the same magnitude. The best estimate of MP4/6-31G**//MP2/6-31G**

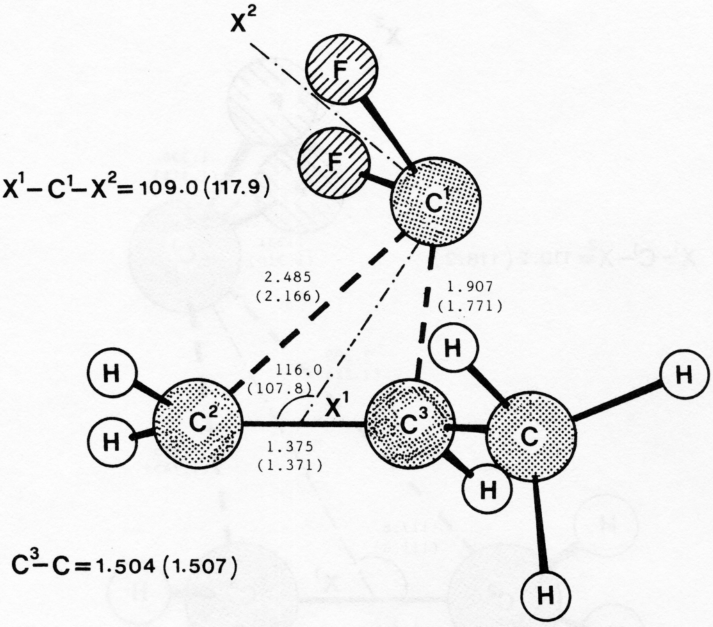

Figure 3. Transition state of the reaction between CF_2 and CH_2CHCH_3, optimized at the MP2 (FU)/6–31G** and HF/6–31G** (in patentheses) levels.

is obtained by applying the additivity relation [Eq. (1)]. By inclusion of ZPVE, the activation barrier and the exothermicity for this reaction are 61 and –168 kJ mol^{-1}, respectively.

For the addition of CF_2 to C_2H_3Cl, the expected Hoffmann TS of C_1 symmetry is obtained again, with the methylene carbon (C^1) being closer to the carbon with the chlorine (C^3) at both HF/6-31G** and MP2/6-31G** levels of optimization. The C^1–C^2 distance is again increased by about 0.3 Å when the calculated geometry is changed from HF/6-31G** to MP2/6-31G** level. Inclusion of correlation effects also reduces the activation energy substantially. When compared with the calculated energies at the HF/6-31G** level, the MP2/6-31G** level reduces the activation barrier by 98 and 73 kJ mol^{-1} for the optimized HF/6-31G** and MP2/6-31G** structures, respectively. At the MP4/6-31G**//MP2/6-31G** level, with inclusion of ZPVE, the activation barrier and the exothermicity of the reaction are 68 and –180 kJ mol^{-1}, respectively.

On examining the TS for the reaction between CF_2 and CH_2CHCH_3, it is seen that it has C_1 symmetry, and the methylene carbon (C^1) is closer to the carbon with the methyl group (C^3). The change of optimized structure from HF/6-31G** to MP2/6-31G** level leads once again to an increase of more than 0.3 Å in the C^1–C^2 distance. When compared with the calculated energies at the HF/6-31G** level, inclusion of correlation effects at the MP2/6-31G** level reduces the activation barrier by 87 and 70 kJ mol^{-1} for the optimized HF/6-31G** and MP2/6-31G** structures, respectively.

TABLE I

Calculated total energies (Hartree)[a]*, with calculated relative energies*[b] *(kJ mol^{-1}) in parentheses, and unscaled zeropoint vibrational energies (kJ mol^{-1}) for the species involved in the reaction of $CF_2 + C_2H_3X$ (X = F, Cl, Me)*

	$CF_2 + C_2H_3X$	TS	Product
X=F, *based on structures optimized at HF/6-31G***			
HF/6-31G**	–236.66074 – 176.88757 (0)	–413.49729 (134)	–413.60931 (–160)
ZPVE	20 + 125	152	165
MP2/6-31G	–236.88448 – 177.11995 (0)	–413.97956 (65)	–414.07849 (–194)
MP2/6-31G**	–237.10966 – 177.32622 (0)	–414.41666 (50)	–414.51497 (–208)
MP4/6-31G	–236.90171 – 177.14817 (0)	–414.02588 (63)	–414.11781 (–178)
MP4/6-31G^{**c}	–237.12689 – 177.35444 (0)	–414.46298 (48)	–414.55429 (–192)
MP4/6-31G^{**d}	(0)	(55)	(–172)
X=F, *based on structures optimized at MP2(FU)/6-31G***			
HF/6-31G**	–236.65897 – 176.88658 (0)	–413.49933 (121)	–413.60724 (–162)
MP2/6-31G	–236.89269 – 177.12388 (0)	–413.99234 (64)	–414.08791 (–187)
MP2/6-31G**	–237.11156 – 177.32731 (0)	–414.41766 (56)	–414.51723 (–206)
MP2(FU)/6-31G**	–237.12047 – 177.33959 (0)	–414.43936 (54)	–414.53979 (–209)
MP4/6-31G	–236.91081 – 177.15246 (0)	–414.03967 (62)	–414.12771 (–169)
MP4/5-31G^{**c}	–237.12968 – 177.35589 (0)	–414.46499 (54)	–414.55703 (–188)
MP4/6-31G^{**d}	(0)	(61)	(–168)
X=Cl, *based on structures optimized at HF/6-31G***			
HF/6-31G**	–236.66074 – 536.93908 (0)	–773.54104 (154)	–773.66358 (–167)
ZPVE	20 + 121	148	161
MP2/6-31G	–236.88448 – 537.09913 (0)	–773.95840 (66)	–774.06211 (–206)
MP2/6-31G**	–237.10966 – 537.33978 (0)	–774.42830 (56)	–774.53365 (–221)
MP4/6-31G	–236.90171 – 537.13127 (0)	–774.09952 (62)	–774.10493 (–189)
MP4/6-31G^{**c}	–237.12689 – 537.37192 (0)	–774.47942 (51)	–774.57647 (–204)
MP4/6-31G^{**d}	(0)	(58)	(–184)
X=Cl, *based on structures optimized at MP2(FU)/6-31G***			
HF/6-31G**	–236.65897 – 536.93851 (0)	–773.54516 (137)	–773.66204 (–170)
MP2/6-31G	–236.89269 – 537.09970 (0)	–773.96612 (69)	–774.06844 (–200)
MP2/6-31G**	–237.11156 – 537.34038 (0)	–774.42770 (64)	–774.53533 (–219)
MP2(FU)/6-31G**	–237.12047 – 537.36045 (0)	–774.45721 (62)	–774.56570 (–223)
MP4/6-31G	–236.91081 – 537.13203 (0)	–774.01763 (66)	–774.11158 (–180)
MP4/6-31G^{**c}	–237.12968 – 537.37271 (0)	–774.47921 (61)	–774.57847 (–200)
MP4/6-31G^{**d}	(0)	(68)	(–180)
X=Me, *based on structures optimized at HF/6-31G***			
HF/6-31G**	–236.66074 – 117.078161 (0)	–353.69390 (127)	–353.81221 (–183)
ZPVE	20 + 223	252	264
MP2/6-31G	–236.88448 – 117.29627 (0)	–354.16449 (43)	–354.26793 (–229)
MP2/6-31G**	–237.10966 – 117.50337 (0)	–354.59764 (40)	–354.70409 (–239)
MP4/6-31G	–236.90171 – 117.33767 (0)	–354.22378 (41)	–354.31987 (–211)
MP4/6-31G^{**c}	–237.12689 – 117 54477 (0)	–354.65693 (39)	–354.75603 (–222)
MP4/6-31G^{**d}	(0)	(48)	(–201)
X=Me, *based on structures optimized at MP2(FU)/6-31G***			
HF/6-31G**	–236.65897 – 117.08112 (0)	–353.69673 (114)	–353.81070 (–185)
MP2/6-31G	–236.89269 – 117.29753 (0)	–354.17420 (42)	–354.27454 (–221)
MP2/6-31G**	–237.11156 – 117.50390 (0)	–354.59879 (44)	–354.70571 (–237)
MP2(FU)/6-31G**	–237.12047 – 117.51908 (0)	–354.62340 (42)	–354.73124 (–241)
MP4/6-31G	–236.91081 – 117.33914 (0)	–354.23426 (41)	–354.32683 (–202)
MP4/6-31G^{**c}	–237.12968 – 117.54551 (0)	–354.65885 (43)	–354.75800 (–217)
MP4/6-31G^{**d}	(0)	(52)	(–196)

[a] All single-point calculations were carried out with the frozen- core (FC) approximation unless otherwise specified.

[b] Calculated with the total energies.

[c] Evaluated using the additivity approximation, Eq. (1) (see text).

[d] Including the HF/6-31G** zero-point vibrationl contribution (scaled down by 0.9).

At the MP4/6-31G**//MP2/6-31G** level, with inclusion of ZPVE, the activation barrier and the exothermicity of the reaction are 52 and –196 kJ mol^{-1}, respectively.

On comparing the activation energies of the three reactions calculated at the MP4/6-31G** level of theory (with inclusion of ZPVE), the barriers have the order of Me < F < Cl. As expected, the electron-donating methyl group leads to a lower barrier than the electron-withdrawing halogens do.[11] On comparing the halogens, due to the more effective $\rho\pi$-$\rho\pi$ back donation of the fluorine in C_2H_3F, the π-electrons are more available in this compound than in C_2H_3Cl.[12] This, in turn, leads to a lower barrier for C_2H_3F than for C_2H_3Cl.

Although the calculated energy barriers follow a trend that agrees with the established concepts in chemistry, it is nonetheless seen that the substituent effect is not very pronounced. At the best level of theory studied so far, *i.e.*, MP4/6-31G**//MP2/6-31G**, the activation barriers for the four reactions $CF_2 + C_2H_3X$, X = H[3], F, Cl, Me, are 57, 61, 68 and 52 kJ mol^{-1}, respectively. In other words, a substitution of H in the ethene by F, Cl or Me causes at the most, a change in the barrier of 11 kJ mol^{-1}. [For comparison, when the substitution is present in carbene rather than in ethene, the change in activation energies is much more notable:[3] the reactions of $CH_2 + C_2H_4$ and $CHF + C_2H_4$ have no energy barrier, while that for $CF_2 + C_2H_4$ is 57 kJ mol^{-1}.] At the same time, the three-membered rings of the four TSs do not much differ from each other.

To conclude, for the four reactions studied previously[3] as well as in the present investigation, there appears to be no significant variation in the energy barriers and structural features in the transition states. Also, as shown previously,[3] correlation effects reduce the activation barriers substantially.

Acknowledgement. – The authors are grateful for the Hong Kong University and Polytechnic Grants Committee grant earmarked for research (account No. 221600080). We also thank the City Polytechnic of Hong Kong for generous allocation of computer time on the CRAY computer located at the San Diego Supercomputer Center.

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12. As a piece of collaborative evidence, we consider the electrophilic aromatic substitution at the *para* position of chlorobenzene and fluorobenzene. The chloro and fluoro groups have comparable inductive effects (-*I*). But, the resonance effect (+*R*) of the fluoro group exceeds that of the chloro group. Hence, the fluoro group's overall substituent effect (-*I*+*R*) surpasses that of the chloro group. For further detail, see, for example, N. S. Isaacs, *Physical Organic Chemistry*, Longman, Essex, 1987, pp. 140–144.

SAŽETAK

Ab initio molekularno orbitalna studija umetanja difluorokarbena u supstituirane etene

Chi-Kin Wong i Wai-Kee Li

Molekulsko-orbitalni računi *ab initio* daju za aktivacijske energije umetanja difluorokarbena u supstituirane etene (C_2H_3X) vrijednosti od 61, 68 i 52 kJ mol^{-1} za X = F, Cl i Me. Ovi rezultati pokazuju da monosupstitucija na etenu nema znatnijeg učinka na aktivacijsku energiju reakcije.