Effects of Fluorination on Methylene Insertion Reactions

Igor S. Ignatyev[†] and Henry F. Schaefer III*

Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602

Received June 26, 1997. Revised Manuscript Received September 17, 1997[⊗]

Abstract: The potential energy surfaces for the insertion reactions of methylene and fluorinated methylenes into the H_2, HF, and F_2 molecules were studied by density functional, many body perturbation, and coupled-cluster theories. These methods predict the barrier for the CF_2 insertion into the hydrogen molecule to be about 33 kcal/mol, that is, significantly lower than previous estimates. A new transition state was found in this system for the reaction path which leads to CHF + HF. However the transition state for this metathesis channel is about 25 kcal/mol higher than that of the insertion channel. For the fluoromethylene insertion into H_2 the predicted activation energy is about 8 kcal/mol. The CH_2 insertion into F_2 proceeds without a barrier. The peculiarity of the insertion reactions between carbenes and HF involves formation of a hydrogen-bonded complex. The $CH_2\cdots HF$ complex is bound by about 10 kcal/mol relative to CH_2 + HF. Coupled-cluster methods predict a small (ca. 3 kcal/mol) barrier for transformation of this complex into CH_3F. However, this barrier lies 7 kcal/mol below reactants CH_2 + HF. In the case of the CHF insertion into HF the analogous barrier is higher and lies ca. 2 kcal/mol above reactants.

Introduction

Insertion of singlet methylene ($^1A_1$) into the hydrogen molecule is a prototype reaction for carbene insertions, and it has been thoroughly studied by theoretical methods.[1−9] The least-motion pathway (within C_{2v} symmetry) for the singlet methylene insertion into H_2 is Woodward-Hoffmann forbidden and requires a significant activation energy.[2] However the path maintaining C_s symmetry has no orbital symmetry restrictions and no barrier at correlated levels of theory.[3]

The substitution of one or two of the hydrogen atoms in methylene by the highly electronegative fluorine atom leads to significant changes in its electronic structure. Fluorine substitution stabilizes the singlet state by widening the HOMO-LUMO gap due to interaction of the fluorine π lone pair orbital and the unoccupied pπ orbital of carbon.[9] While in CH_2 the ground state is of $^3B_1$ symmetry and the singlet-triplet gap is 9.0 kcal/mol (experimental value[10]), in CHF the ground state becomes $^1A'$ and the triplet state ($^3A''$) lies at 14.9 kcal/mol.[11] For CF_2 the singlet-triplet gap grows to 57 kcal/mol.[12] The inverted order of stability of the triplet and the singlet states in fluorinated

carbenes compared to CH_2 results in the appearance of an activation barrier for the insertion reactions of CF_2 ($^1A_1$) into σ bonds.[9,13] This was confirmed experimentally by Battin-Leclerc, Smith, Hayman, and Murrells[14] in 1996 for the system CF_2 + H_2.

The barriers for the reactions CF_2 + H_2 → CH_2F_2 and CHF + H_2 → CH_3F were estimated by Sosa and Schlegel[9] in 1984. Their single point MBPT calculations (up to MP4) at the optimized SCF geometries employing the 6-31G* basis set gave barriers in the 45−47 kcal/mol range for the CF_2 insertion and 14−15 kcal/mol for CHF (enthalpies at 0 K).

Since the Sosa-Schlegel work was published, there have appeared new methods in quantum chemistry which consistently predict reaction thermochemistry with reliability. Among these, two groups of methods should be mentioned. First, and most reliable, are those based on coupled-cluster theory,[15,16] and second are the hybrid Hartree-Fock/density functional theory (DFT) methods.[17] The coupled-cluster method which includes all single and double excitations (CCSD), and especially its version with a perturbative treatment of triples (CCSD(T)), in conjunction with relatively large basis sets provide excellent reliability for geometrical parameters, enthalpies of formation, and vibrational frequencies.[15] The DFT methods, especially those which combine Becke's three-parameter hybrid exchange functional (B3)[18] with various correlation functionals, give surprisingly good results in the prediction of the equilibrium thermochemical parameters.[19−22] They have an important

† Permanent address: Institute for Silicate Chemistry, Russian Academy of Sciences, Odoevskogo 24, c.2, 199155, St. Petersburg, Russia.
⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1997.
(1) Dobson, R. C.; Hayes, D. M.; Hoffmann, R. *J. Am. Chem. Soc.* **1971,** *93,* 6188.
(2) Bauschlicher, C. W.; Schaefer, H. F.; Bender, C. F. *J. Am. Chem. Soc.* **1976,** *98,* 1653.
(3) Bauschlicher, C. W.; Haber, K.; Schaefer, H. F.; Bender, C. F. *J. Am. Chem. Soc.* **1977,** *99,* 3610.
(4) Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1979,** *51,* 207.
(5) Borden, W. T.; Davidson, E. R. *Annu. Rev. Phys. Chem.* **1979,** *30,* 125.
(6) Cain, S. R.; Hoffmann, R.; Grant, E. R. *J. Phys. Chem.* **1981,** *85,* 4046.
(7) Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.* **1984,** *106,* 5421.
(8) Sironi, M.; Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Am. Chem. Soc.* **1990,** *112,* 5054.
(9) Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1984,** *106,* 5847.
(10) Leopold, D. G.; Murray, K. K.; Miller A. E. S; Lineberger W. C *J. Chem. Phys.* **1985,** *83,* 4849. Bunker, P. R.; Sears, T. J. *J. Chem. Phys.* **1985,** *83,* 4849.
(11) Gilles, M. K.; Ervin, K. M.; Ho, J; Lineberger, W. C. *J. Phys. Chem.* **1992,** *96,* 1130.
(12) Koda, S. *Chem. Phys. Lett.* **1978,** *55,* 353. McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983,** *79,* 5251.

(13) Bach, R. D; Su M.-D.; Aldabbagh, E.; Andrés, J. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1993,** *115,* 10237.
(14) Battin-Leclerc, F.; Smith, A. P.; Hayman, G. D.; Murrells, T. P. *J. Chem. Soc., Faraday Trans.* **1996,** *92,* 3305.
(15) Bartlett, R. J. *J. Phys. Chem.* **1989,** *93,* 1697 and references therein.
(16) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, 1995; pp 47−108.
(17) Kohn, W.; Becke, A. D.; Parr R. G. *J. Phys. Chem.* **1996,** *100,* 12974.
(18) Becke, A. D. *J. Chem. Phys.* **1993,** *98,* 5648.
(19) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997,** *106,* 1063.
(20) Bauschlicher, C. W. *Chem. Phys. Lett.* **1995,** *246,* 40.
(21) Durant, J. L. *Chem. Phys. Lett.* **1996,** *256,* 595.
(22) Glukhovtsev, M. N.; Bach, R. D.; Pross, A.; Radom L. *Chem. Phys. Lett.* **1996,** *260,* 558.

advantage being much less computationally demanding but lack the theoretical consistency of the coupled-cluster theory methods. With these hybrid HF/DFT methods the combination of the B3 functional with the Lee-Yang-Parr nonlocal correlation functional (LYP)[23] gives average absolute deviations with respect to experimental data for the enthalpies of formation approaching those achieved by the G2 method. We note especially in this regard the recent systematic study of 148 molecules by Curtis et *al.*[19] However, the maximum deviations for the B3LYP method are significantly larger.

Much less is known about the performance of different methods in predicting the activation barriers for chemical reactions. There is no extensive systematic study of the coupled-cluster methods, but one expects that, being the theoretically consistent methods, they may approach the exact values for barrier heights. On the other hand, there are some systematic studies of the DFT method's performance in reproducing reaction barriers.[21,22] The general opinion is that the B3LYP method tends to underestimate barrier heights. However, Durant[21] found that Becke's half-and-half exchange functional with the LYP correlation treatment (BHLYP), as implemented in GAUSSIAN 92/DFT,[24] is less affected by this problem and gives the best estimates of reaction barrier heights among several DFT methods.

Although the main goal of this work is to examine the effect of fluorine substitution in methylene on the singlet insertion reactions into H_2, other reactions of carbenes which result in formation of CH_2F_2 were also studied. These include the insertion of methylene into F_2 and the reaction between CHF and HF. The potential energy surfaces for these reactions have not been previously examined to the best of our knowledge. For the CH_3F system the $CH_2 + HF$ and $CHF + H_2$ reactions were also studied here. Some aspects of the potential surface of this reaction were studied earlier by Pople[25] and by Yates, Bouma, and Radom.[26]

Theoretical Approach

Two hybrid DFT methods were used in this work, the first being B3LYP method as implemented in the GAUSSIAN 94 program.[27] In this method the exchange functional was constructed by Becke from three functionals including the Hartree-Fock exchange functional, while the correlation functional is that of Lee, Yang, and Parr. The other method used here is BHLYP, in which the hybrid exchange functional is built from 50% exact exchange and 50% Slater exchange.[21] This method was used as realized in the GAUSSIAN 92/DFT[24] program. Theoretical methods employed here also involved second-order Moller−Plesset perturbation theory with all electrons correlated (MP2),[28] the quadratic configuration interaction

method including single and double excitations with core electrons excluded from correlation treatment (QCISD),[29] the coupled-cluster method including all single and double excitations (CCSD),[30] and the latter including all connected triple excitations perturbatively (CCSD(T)). In the coupled-cluster methods all electrons were correlated.[31] These methods were employed as they are realized in the programs GAUSSIAN94[27] (MP2, QCISD) and ACESII.[32]

The basis sets employed were of DZP quality, constructed from the standard double-ζ set of Huzinaga and Dunning[33] [C,F (9s5p/4s2p) and H (4s/2s)] with the addition of six d-like functions to the carbon atoms with orbital exponent $\alpha_d(C) = 0.75$, to the fluorine atoms with exponent $\alpha_d(O) = 1.00$ and a set of p functions on hydrogens ($\alpha_p(H) = 0.75$). Pople's standard 6-311G** basis set[34] was also used.

Geometries of reactants, transition states, and products were fully optimized, and vibrational frequencies (ZPVE) were evaluated at the same level of theory unless otherwise stated.

Results and Discussion

1. The $CF_2 + H_2$ System. The transition state for insertion of CF_2 into the hydrogen molecule found in 1984 by Sosa and Schlegel[9] at the SCF level was a starting point for our study of this reaction by correlated methods. The optimized geometries for stationary points on this surface are presented in Table A. Note that all tables are included in the Supporting Information.

The experimental geometrical parameters for the reactants and the product of the $CF_2 + H_2$ reaction are known. The structural parameters of difluoromethylene were refined by Kirchhoff and Lide[35] from their microwave spectrum to be $r(CF) = 1.303 \pm 0.0001$ Å and $\angle FCF = 104.78 \pm 0.02°$. This is an average or r_z structure, which in the case of a perfectly harmonic potential would coincide with the equilibrium r_e structure. Assuming that the anharmonicity of CF_2 vibrations is not very high, we may expect r_e values to be close to those of the r_z structure. It is interesting to note that the closest agreement with experiment is achieved by B3LYP, while the MP2 and coupled-cluster methods slightly overshoot the CF bond length (by 0.010 and 0.014 Å, respectively, Table A). With larger basis sets, of course, we expect the CCSD(T) method to be the most reliable. For the CH_2F_2 molecule, where both r_z and r_e structures have been experimentally refined,[36] all methods (with the exception of BHLYP) predict a CF bond length which is very close to the r_z value but disagrees considerably with the r_e structure. However there are some doubts about the accuracy of the estimation of this parameter in the experimental r_e structure.[36] One might expect the significant shortening of the highly anharmonic CH bond in the r_e structure but the almost 0.01 Å decrease in the CF bond seems surprising. Possibly

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

(24) Gaussian 92/DFT, Revision F.2; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1993.

(25) Pople J. A. *Chem. Phys. Lett.* **1986**, *132*, 144.

(26) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2250.

(27) Gaussian 94, Revision B.1; 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. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(28) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(29) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(30) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *89*, 7382.

(31) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(32) Stanton, J. F.; Gauss, J.; Lauderdale, W. J.; Watts, J. D.; Bartlett, R. J. ACES II. The package also contains modified versions of the MOLECULE Gaussian integral program of J. Almlöf and P. R. Taylor, the ABACUS integral derivative program written by T. U. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and P. R. Taylor, and the PROPS property evaluation integral code of P. R. Taylor.

(33) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 3, pp 1−27.

(34) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(35) Kirchhoff, W. H.; Lide, D. R. *J. Mol. Spectrosc.* **1973**, *47*, 491.

(36) Hirota, E. *J. Mol. Spectrosc.* **1978**, *69*, 409.
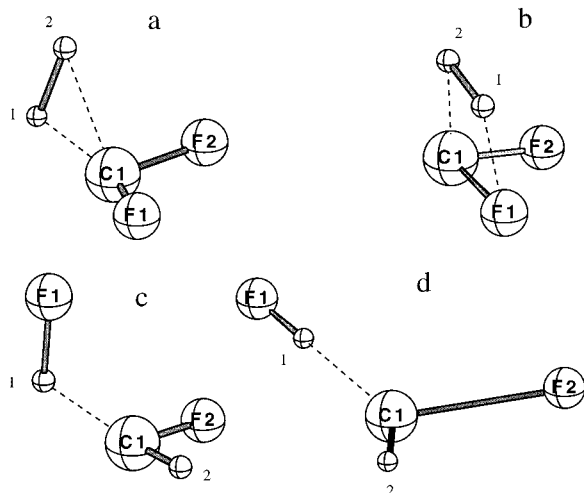
Figure 1. Structures of transition states (a–c) and the CHF···HF hydrogen-bonded complex (d) in the CH_2F_2 system.

the r_e parameters derived from experimental data are not of high accuracy, perhaps due to a poor choice of anharmonic force constants used in this procedure.

The heat of reaction for the addition of CF_2 to H_2 is the only known thermochemical parameter for this system. The experimental estimate in Table B is derived from $\Delta H_f^o(0\ K)$ values for CF_2 (43.6 ± 1.5 kcal/mol) and CH_2F_2 (105.9 ± 0.4 kcal/mol) reported in ref 37. The MP2(61.8) and B3LYP(61.3) methods give better agreement with the experimental (62.3 ± 1.9 kcal/mol) value than the coupled-cluster (58.7 for CCSD; CCSD(T) gives 57.4) methods, but the accuracy of the experimental value determination is not high.

The transition state found at the SCF level by Sosa and Schlegel[9] was a starting point for its refinement by correlated methods. This transition state has C_s symmetry with a relatively short CH1 bond (1.16 Å) formed by the carbon lone pair of electrons (Figure 1a). It is interesting to note that the length of this bond does not change significantly with inclusion of electron correlation (Table A). The other carbon–hydrogen distance (1.6 Å) is too long to be considered a conventional bond, and the population analysis shows a negative value for this pair of atoms. Following the reaction path from this transition state by the intrinsic reaction coordinate (IRC) method (B3LYP/DZP) shows that it goes to CH_2F_2 in the forward direction and to $CF_2 + H_2$ in the reverse direction. The latter path was traced to a distance between the carbon and hydrogens of 3.0 Å. It cannot be excluded that there exists some very weakly bound complex beyond this distance, but such a species should have a well depth less than 0.5 kcal/mol and has a tendency to disappear with the increase of the quality of the theoretical method, as mentioned by Sosa and Schlegel.[9]

The barrier height (30.3 kcal/mol) for the transition state for the singlet CF_2 insertion into H_2 obtained at the B3LYP level (Table B) is significantly lower than those estimated by Sosa and Schlegel.[9] However, the general trend of the B3LYP method to underestimate barrier heights is well-known, and it suggests that this B3LYP value is a lower limit. The BHLYP value (34.9 kcal/mol) is higher, as expected, and it is closer to those predicted by the correlated methods. The increase of the quality of the method with the same basis set (DZP) shows a tendency toward the steady lowering of this barrier, but the use of the 6-311G** basis set leads to an increase (Table C). Taking into account these tendencies we can predict the barrier height for the $CF_2 + H_2$ insertion reaction to be 34 ± 3 kcal/mol.
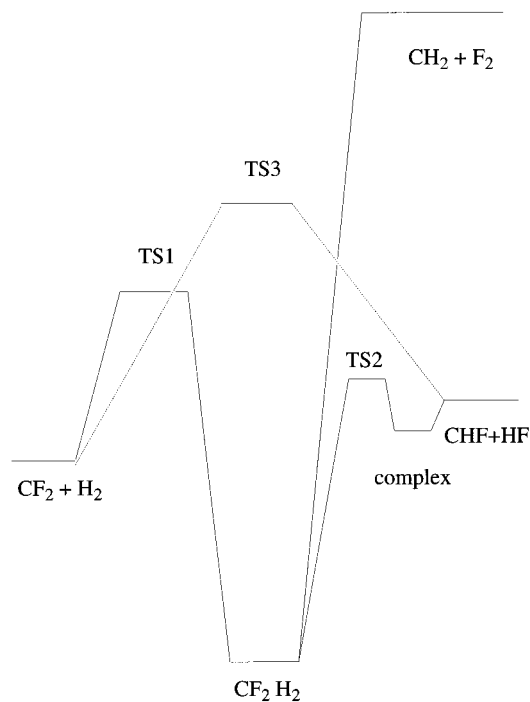
A new transition state was found when the search was not restricted by the symmetry plane. This transition state (Figure
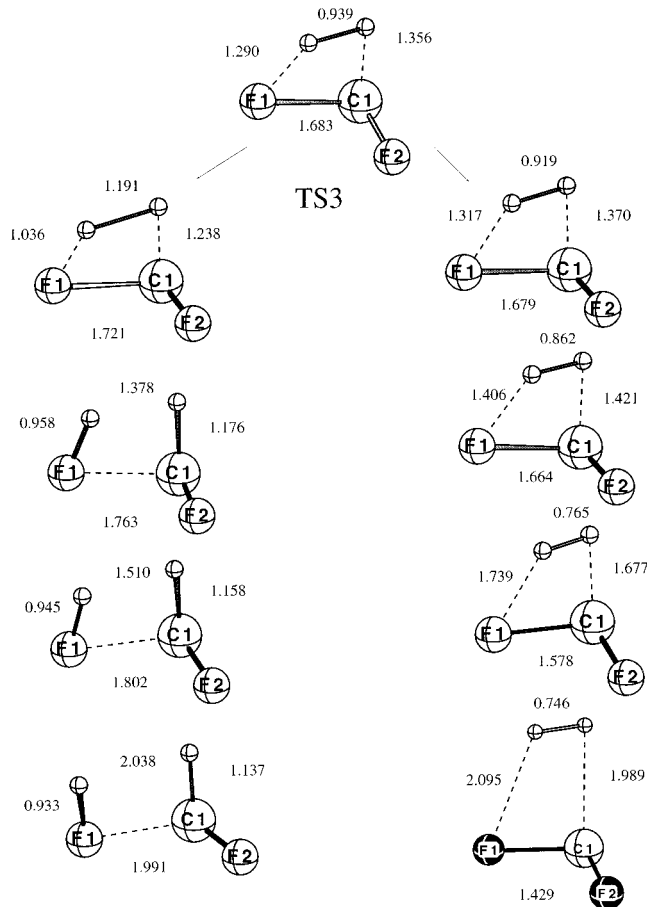
Figure 2. Some points on the intrinsic reaction coordinate (IRC) for the metathesis reaction $CF_2 + H_2 \rightleftharpoons CHF + HF$. Results from the B3LYP/DZP level of theory.

1b) is characterized by a strong interaction with both hydrogens, one with the carbon atom and the other with fluorine. The hydrogen molecule resides above the CF bond of CF_2, significantly perturbing the latter. The optimized geometrical parameters of this transition state (TS3) are presented in Table C. The IRC procedure shows that descending from TS3 leads to CHF + HF (Figure 2). Thus this transition state refers to the metathesis reaction $CF_2 + H_2 \rightleftharpoons CHF + HF$. To the best of our knowledge this reaction has not been discussed in the literature. The barrier height for this reaction, however, is significantly higher than that for formation of CH_2F_2 (Figure 3).

2. The CHF + HF → CH_2F_2 Reaction. Insertion of singlet fluorocarbene into hydrogen fluoride has not been studied previously by theoretical methods. However, the studies of Pople[24] and of Yates, Bouma, and Radom[26] have shown that in contrast to the case of insertion of carbenes into H_2, a hydrogen-bonded complex is formed between methylene and HF. Our study confirmed the formation of such a complex in the case of fluoromethylene (Figure 1d). The depth of this local minimum is about 10 kcal/mol and shows no tendency to disappear as the level of theory is raised (Table D). However, the distance between carbon and the proton of HF tends to lengthen with the increase of level of theory from 1.788 Å (B3LYP) to 1.867 (CCSD(T)) (Table E). Thus the CHF···HF system is best described as a strong hydrogen bond. Note also the shortening of the CH and CF bonds in the CHF moiety of the complex compared to free fluorocarbene. Analysis of the Mulliken populations shows that there is charge transfer from the fluorine of CHF to that of HF in the complex. This may reduce the destabilizing donation of the CHF fluorine lone pairs into the pπ orbital of carbon. The transition state (TS2) for

Effects of Fluorination on Methylene Insertion Reactions

J. Am. Chem. Soc., Vol. 119, No. 50, 1997 12309

Figure 3. The energetic scheme for the stationary points of the CH_2F_2 system.

Figure 4. Structures of two types of transition states for the CH_2 insertion into F_2. These transition states reflect the *syn* (a) and *anti* (b) orientations of the F_2 molecule with respect to the CH_2 lone pair.

transformation of this complex to CH_2F_2 was found at the B3LYP level to be 7.9 kcal/mol below reactants and 4.4 kcal/mol above the $CHF\cdots HF$ complex (Figure 1c). The BHLYP and MP2 methods predict significantly higher barriers but still slightly below the reactants in energy (Table D). Implementation of the coupled-cluster methods significantly increases the barrier heights [to 4.5 kcal for CCSD and 1.7 kcal for CCSD-(T)]. Thus, the best estimate of the enthalpy of the transition state for the rearrangment of the hydrogen-bonded complex into CH_2F_2 is about 10 kcal above the complex and about 3 kcal/mol above reactants.

3. The $CH_2 + F_2 \rightarrow CH_2F_2$ Reaction. This is the third plausible reaction on this hypersurface to form CH_2F_2. It has not been investigated previously to the best of our knowledge by theoretical methods. For the analogous reaction of SiH_2 two transition structures (corresponding to the *syn* and *anti* configurations of F_2 relative to the SiH_2 lone pair) were found by Schlegel and co-workers[38] recently at the SCF level of theory. However, at correlated levels no barrier was found for the *anti* SiH_2 approach, and the barrier for the *syn* approach was only 0.5 kcal/mol above reactants at the QCISD/6-31G* level.

Two analogous transition states were found here for methylene insertion into the fluorine molecule at the SCF/DZP level. One of them (TS1, Figure 4a) corresponds to formation of a bond through donation of electrons of one fluorine to the vacant p-orbital of C with *syn* orientation of the F-F bond to the methylene lone pair. The other structure (TS2, Figure 4b) has a F-F bond *anti* to this lone pair. However, introduction of electron correlation usually leads to the disappearance of these transition states. Two of the methods (BHLYP and MP2) still give small barriers (2.4 and 2.9 kcal/mol, respectively) for this reaction, although significantly lower than at the SCF level (Table F). All other methods employed predict the absence of a barrier for this reaction. It is worth noting that the methods which predict the existence of a small barrier show the poorest
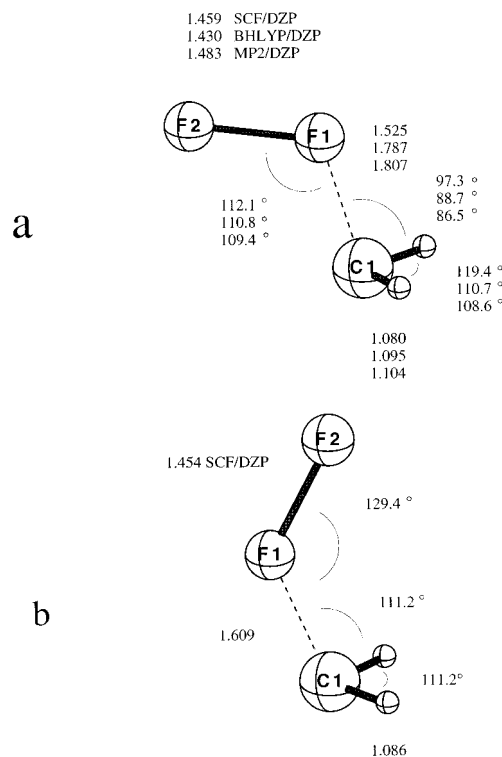
description of the experimental reaction enthalpy. The fair description of the enthalpy by the SCF method may be due to a fortuitous cancellation of errors.

4. The $CHF + H_2$ System. Insertion of fluorocarbene into the hydrogen molecule should have a lower barrier than that for CF_2. Sosa and Schlegel[9] have found a transition state for this process at the SCF/6-31G* level. Their MP4 energy calculation at the SCF optimized geometry gave a barrier height of about 10 kcal/mol. Wong, Li, and Baker[39] employed several DFT methods for predicting the barrier height of this reaction, and they concluded that the small negative barriers (E_0 values) which they obtained with the BLYP and B3P86 functionals is "clearly unphysical and must raise a question mark over the use of these particular functionals for reactions with low barrier".[39]

Implementation of the B3LYP functional with the DZP basis set in this work gave a very small negative barrier height (-0.4 kcal/mol, Table G). The structure of the transition state corresponding to this barrier is depicted in Figure 5b. The BHLYP/DZP method gives a small (2.2 kcal) but positive E_0 barrier height, while MP2(full)/DZP increases its value to 4.6 kcal/mol. The problem with negative barrier heights was solved when we used the intrinsic reaction coordinate (IRC) technique to descend from the saddle point. On one side it goes to the global minimum CH_3F, but on the other we found a local minimum which corresponds to the loose complex between CHF and H_2 (Figure 5a). The subsequent optimization of the geometry of this complex by different methods showed that the corresponding minimum is very shallow and that the $C\cdots H$ distance tends to increase with the level of theory (to 1.131 Å with the CCSD(T) method, Table H). The dissociation energies

(37) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*.

(38) Ignacio, E. W.; Schlegel, H. B. *J. Chem. Phys.* **1992**, *96*, 1620. Ayala, P. Y.; Schlegel, H. B. *Chem. Phys. Lett.* **1994**, *225*, 410.
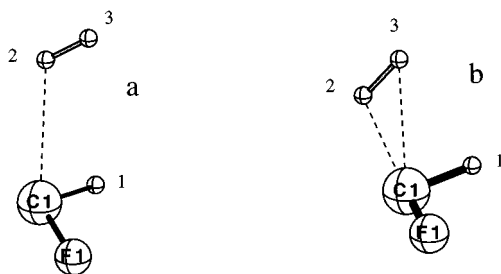
(39) Wong, C.-K.; Li, W.-K.; Baker, J. *J. Mol. Struct. (Theochem)* **1995**, *357*, 75.a.

(40) Suzuki, T; Saito, S; Hirota, E. *J. Mol. Spectrosc.* **1981**, *90*, 447.

(41) Huber, K. P.; Herzberg, G. Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules; Van Nostrand: New York, 1979.

Figure 5. Structures of the complex (a) and transition state (b) for the CHF insertion into H_2.

Figure 6. Structures of the complex (a) and transition state (b) for the CH_2 insertion into HF.

Figure 7. The energetic scheme for the stationary points of the CH_3F system.

for this complex decrease from 1.0 kcal/mol (B3LYP/DZP) to 0.4 kcal/mol (QCISD/6-311G**). However the presence of this minimum gives physical sense to the "negative barrier heights". The lowest vibrational frequency of the complex also decreases from 96 cm^{-1} (B3LYP/DZP) to 22 cm^{-1} (QCISD/6-311G**) with the level of theory.

Despite the fact that the height of the barrier for the insertion of CHF into H_2 is very small with the HF/DFT methods, the barrier increases when the coupled-cluster methods are applied. With the coupled-cluster methods the barrier varies from 8.2 to 10.3 kcal/mol (ΔH_0, Table H). Thus we consider 7 kcal/mol as a fair estimate of this barrier height.

5. CH_2 + HF → CH_3F. Addition of singlet methylene to hydrogen fluoride was previously studied by Pople[25] and by Yates, Bouma, and Radom.[26] In both studies geometrical optimizations were performed at the MP2/6-31G* level. The hydrogen-bonded complex $H_2C\cdots HF$ was found to be a local minimum on the CH_2 + HF potential energy surface of 8.6 kcal/mol depth relative to reactants. However the barrier for its rearrangement into the CH_3F corresponding to the global minimum is less than 1 kcal/mol[26] and is hardly significant.

Our scanning of the CH_2 + HF potential energy surface with the help of the DFT and CC methods gave similar results. At all levels of theory the hydrogen-bonded complex (Figure 5c) exists as a local minimum. However, its relative energy decreases from −11.3 kcal/mol at B3LYP to −6.6 kcal/mol at QCISD (Table I). The $C\cdots H$ distance correspondingly grows from 1.749 to 1.942 Å (Table J). Thus the $CH_2\cdots HF$ hydrogen bond is perhaps 30% stronger than that for the water dimer. The transition state for the rearrangement of this complex into CH_3F was found at all levels of theory (Figure 5d; geometrical parameters—Table J). There is a difference between the geometry and energy of this transition state obtained with the B3LYP method and those from other methods employed. The B3LYP geometry is close to that of the complex, and its barrier height is vanishingly small (0.2 kcal/mol, Table I). Other methods predict a "later" geometry and a higher (although not exceeding 4.4 kcal/mol, the CCSD result; CCSD(T) gives 2.8 kcal) barrier. Still, this small barrier lies below the energy level of the reactants, thus making the reaction CH_2 + HF → CH_3F effectively barrierless (Figure 6).

Conclusions

1. The barrier height for insertion of CF_2 into H_2 was found to be about 10 kcal/mol lower than predicted earlier via SCF optimized geometries. The enthalpy of activation varies from 30 kcal/mol (B3LYP/DZP) to 36 kcal/mol (CCSD(T)/DZP).

2. The previously unknown transition state for the metathesis reaction CF_2 + H_2 ⇌ CHF + HF was found to lie about 60 kcal/mol above CF_2 + H_2 and about 50 kcal/mol above CHF
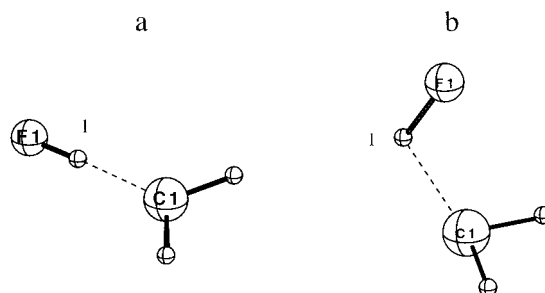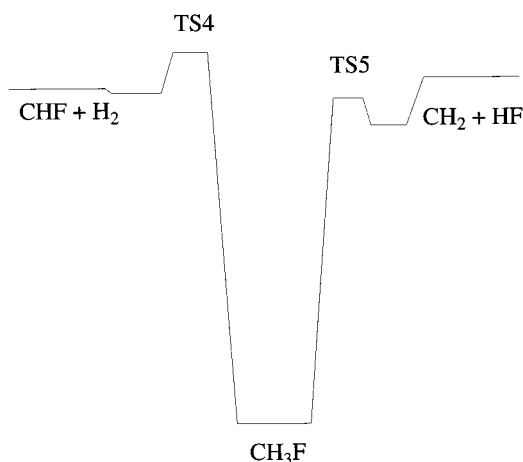
+ HF. These results are consistent with the 1996 experiments of Battin-Leclerc and co-workers.[14]

3. An enthalpy of activation of about 8 kcal/mol (ΔH_0) was found for the insertion of CHF into H_2 at coupled-cluster levels. The loosely bound complex between CHF and H_2 has a dissociation energy D_e less than one kcal/mol at higher levels of theory.

4. For the CH_2 + F_2 → CH_2F_2 reaction transition states were found for BHLYP (5.6 kcal/mol) and MP2 (6.0 kcal/mol). All other methods employed predict the absence of the barrier for this reaction. The reaction is predicted to be barrierless.

5. Insertion of CHF and CH_2 into HF proceeds through formation of hydrogen-bonded complexes of C_{2v} symmetry. A transition state of ca. 10 kcal/mol above this complex and about 2 kcal/mol above reactants was found in the CHF + HF reaction by the coupled-cluster methods. All methods except Hartree−Fock theory predict a very low (less than 5 kcal/mol above the complex) barrier for the CH_2 insertion into HF. This transition state, however, lies below reactants, so the CH_2 + HF → CH_3F reaction is predicted to be effectively barrierless.

Supporting Information Available: Tables of theoretical and experimental parameters, total energies, and theoretical geometrical parameters (10 pages). See any current masthead page for ordering and Internet access instructions.