

Ab Initio Molecular Orbital Studies of H + C₂H₄ and F + C₂H₄. 2. Comparison of the Energetics

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Heats of reaction and barrier heights have been computed for H + C₂H₄ ⇌ C₂H₅ and F + C₂H₄ → C₂H₄F → H + C₂H₃F by using Møller-Plesset perturbation theory up to fourth order with the 3-21G and 6-31G* basis sets and correcting for zero-point energy. Although energy differences and activation energies for these reactions are difficult to compute directly, reliable comparisons can be made: the CH bond dissociation energy for C₂H₄F is 4.1 ± 0.5 kcal/mol less than C₂H₅ and the exit channel barrier for C₂H₄F → H + C₂H₃F is 3.5 ± 0.5 kcal/mol larger than for C₂H₅. By combining these and related calculations with experimental data, the following estimates are obtained: the heat of reaction for F + C₂H₄ → H + C₂H₃F, -15 ± 2 kcal/mol; the CH bond dissociation energy for C₂H₄F, 31.4 ± 1 kcal/mol; and the exit channel barrier for C₂H₄F → C₂H₃F + H, 5.6 ± 0.5 kcal/mol. The implications for the dynamics of the F + C₂H₄ reaction are discussed.

Introduction

In the gas phase, hydrogen and fluorine react exothermally with ethylene to produce the intermediate ethyl¹ and β-fluoroethyl² radicals. These intermediates are formed with 40–50 kcal/mol excess internal energy and decompose to ethylene and fluoroethylene unless collisionally stabilized.^{1–4} In a previous paper⁵ (part 1), the equilibrium geometries, vibrational frequencies, and location of the transition structures were examined at several different calculational levels. The energetics of the reaction surfaces are considered in the present work and the implications for the reaction dynamics are discussed.

Experimental information on the details of these radical formation and decomposition reactions are available from molecular beam,^{4,6} classical chemical kinetics,^{7–9} and infrared chemiluminescence studies.¹⁰ Theoretical work includes molecular orbital calculations,^{11–15} statistical kinetic treatments,^{6–9,16–19} and dynamical studies.^{15,19–22}

For the H + C₂H₄ ⇌ C₂H₅ reaction, a detailed potential energy surface has been constructed by using minimal and extended basis set ab initio calculations.¹¹ A relatively tight transition structure and a low barrier for H atom addition were found. Molecular dynamics studies on this surface indicate that recrossing of the dividing surface between reactants and products is unimportant for H + C₂H₄ recombination.²¹ Nearly the same transition structures and energy differences were found by Nagase and Kern¹² using fully optimized UHF/4-31G calculations. Higher level molecular orbital calculations that include extensive configuration interaction have been carried out by Harding¹³ and also predict a small barrier to addition with a transition structure similar to that above. The barrier to 1,2 hydrogen migration was calculated to be ca. 5 kcal/mol higher than the CH dissociation barrier.¹³

A major controversy has arisen over the thermal kinetics for the H + C₂H₄ ⇌ C₂H₅ system. If conventional activated complex theory²³ is used, the activated complex that fits the C₂H₅ decomposition rate overestimates the H + C₂H₄ recombination rate by an order of magnitude.⁸ This problem has been probed with classical trajectory calculations, but no conclusive answers are found.^{20–22} The dilemma has recently been resolved²⁴ by using a revised value for the ethyl radical heat of formation combined with

ab initio calculations of the geometry and vibrational frequencies for the transition state.⁵ Activated complex theory rate constants now agree with experiment for both the recombination and the dissociation rates.

Lee and co-workers^{4,6} have examined the F + CH₂CH₂ reaction using crossed molecular beam experiments. From the angular distribution of products, they conclude that the intermediate fluoroethyl radical has a relatively long lifetime (i.e., several rotational periods). Measurement of the recoil energy distributions indicate that approximately 50% of the total available energy appears as relative kinetic energy of the H + C₂H₃F products, independent of initial relative translational energy in the range of 2–12 kcal/mol. From infrared chemiluminescence experiments, McDonald

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TABLE I: Total Energies^a for the Reactions $F + C_2H_4 \rightarrow C_2H_4F \rightarrow H + C_2H_3F$

level	F + C ₂ H ₄	F-C ₂ H ₄ ^b	C ₂ H ₄ F ^c	H-C ₂ H ₃ F ^b	H + C ₂ H ₃ F
HF/3-21G	-176.445 997	-176.441 218	-176.475 827	-176.407 410	-176.416 769
MP2/3-21G	-176.703 478	-176.696 042	-176.751 067	-176.685 895	-176.710 219
MP3/3-21G	-176.724 172	-176.715 948	-176.766 608	-176.698 457	-176.720 570
MP4/3-21G	-176.731 553	-176.726 459	-176.775 708	-176.710 058	-176.730 763
HF/6-31G*	-177.396 676	-177.390 952	-177.443 146	-177.370 310	-177.380 184
MP2/6-31G*	-177.771 618	-177.771 612	-177.845 716	-177.775 715	-177.800 366
ZPE ^d	34.57	34.18	35.29	30.36	30.11

^a Total energies in atomic units; 1 au = 627.51 kcal/mol. ^b Transition structure. ^c Gauche conformations. ^d Zero-point energy in kcal/mol.

and co-workers find that the C₂H₃F vibrational energy distribution is nonstatistical.¹⁰ Classical trajectory calculations by Hase and Bhalla²² indicate that the large and constant fraction of energy released as relative translation is a result of the exit channel barrier, of which ~80% goes to translation, and the conservation of orbital angular momentum during the dissociation event which nonstatistically apportions the available energy to relative translation. Vibrational adiabaticity in the exit channel may also influence the product energies.^{17,18}

Kato and Morokuma¹⁵ have used ab initio molecular orbital (MO) calculations to examine the decomposition of the fluoroethyl radical. Geometries, relative energies, and vibrational frequencies have been determined for the complex, transition structure, and products at the SCF level with a split valence basis set. The region of the energy surface between reactants and complex has also been examined with MO methods. Clark et al.¹⁴ have found a loose transition structure with a small barrier for the addition of fluorine to ethylene. No calculations have appeared in the literature that go beyond the UHF/4-31G level for the $F + CH_2CH_2 \rightarrow H + FCHCH_2$ system.

The aim of the work reported here is to obtain reliable energetics for the $F + C_2H_4 \rightarrow C_2H_4F \rightarrow H + C_2H_3F$ reaction from ab initio calculations. Both the effect of basis set and electron correlation are considered in the computations. It is hoped that the results of this study will provide an important reference point in interpreting the F and H plus ethylene reaction dynamics.

Method

Ab initio calculations were carried out with the GAUSSIAN 80 series of programs²⁵ using extended (3-21G) and polarization (6-31G*) basis sets.²⁶ The latter is an extended basis set augmented by a set of 6 d functions on each non-hydrogen atom. Equilibrium geometries and transition structures were discussed in a previous paper.⁵ They were fully optimized at the Hartree-Fock level with both basis sets, HF/3-21G and HF/6-31G*, by using an analytical gradient procedure. For the $F + C_2H_4 \rightarrow C_2H_4F \rightarrow H + C_2H_3F$ system, several additional structures along the reaction path were optimized at the HF/6-31G* level by fixing the elongated C-F or C-H bond and minimizing the energy with respect to all the other coordinates.

Configuration interaction and Møller-Plesset perturbation theory were used to calculate correlation energy. The reference configuration was a single determinantal unrestricted Hartree-Fock (UHF) wavefunction and the frozen-core approximation (no excitation out of the core

TABLE II: Total Energies^a for the Reaction $H + C_2H_4 \rightleftharpoons C_2H_5$

level	H + C ₂ H ₄	H-C ₂ H ₄ ^b	C ₂ H ₅
HF/3-21G	-78.097 189	-78.093 569	-78.163 645
MP2/3-21G	-78.276 313	-78.258 967	-78.327 790
MP3/3-21G	-78.293 209	-78.277 457	-78.348 778
MP4/3-21G	-78.299 805	-78.285 315	-78.354 605
CISD/3-21G	-78.288 189 ^c	-78.278 044	-78.345 167
HF/6-31G*	-78.529 952	-78.525 323	-78.597 148
MP2/6-31G*	-78.782 578	-78.763 766	-78.835 367
MP3/6-31G*	-78.803 594	-78.787 183	-78.861 566
MP4/6-31G*	-78.808 786	-78.794 058	-78.866 696
ZPE ^d	34.57	34.75	39.68

^a Total energies in atomic units. ^b Transition structure. ^c CISD based on UHF single determinant for the structure with H at 5 Å from C and perpendicular to the ethylene plane. The UHF, UMP2, and UMP3 energies at this geometry are within 10⁻⁶ au of infinitely separated hydrogen and ethylene (restricted wave function). ^d Zero-point energy in kcal/mol.

orbitals) was used throughout. With the smaller basis set, it was possible to carry out configuration interaction including all single and double excitations²⁷ (CISD) as well as fourth order Møller-Plesset perturbation theory including all single, double, and quadruple excitations²⁸ (MP4). For the larger 6-31G* basis set, only second-order perturbation theory (MP2/6-31G*) could be used for the three heavy atom molecules.

Approximations to the MP3/6-31G* and MP4/6-31G* total energies were obtained by scaling the Møller-Plesset contributions to the energy at the 3-21G level, so that the scaled MP2/3-21G correlation energy equals the calculated MP2/6-31G* correlation energy:

$$\begin{aligned} \text{estimated } E(\text{MP}_n/6-31G^*) &= \\ & E(\text{HF}/6-31G^*) + \lambda[E(\text{MP}_n/3-21G) - E(\text{HF}/3-21G)] \\ \lambda &= [E(\text{MP}_2/6-31G^*) - \\ & E(\text{HF}/6-31G^*)]/[E(\text{MP}_2/3-21G) - E(\text{HF}/3-21G)] \end{aligned}$$

Although the third- and fourth-order Møller-Plesset contributions to the 6-31G* energies are overestimated somewhat by this method, the energy differences obtained from the estimated MP3/6-31G* and MP4/6-31G* total energies agree well with the directly computed values (cf. Table III: $F + CH_4 \rightarrow H + CH_3F$; Table IV: $C_2H_5 \rightarrow H + C_2H_4$; Table V: $H + C_2H_4$ barrier).

Results and Discussion

The total energies for the stationary points on the surfaces for $H + C_2H_4 \rightleftharpoons C_2H_5$ and $F + C_2H_4 \rightarrow C_2H_4F \rightarrow H + C_2H_3F$ are collected in Tables I and II. The HF/3-21G,

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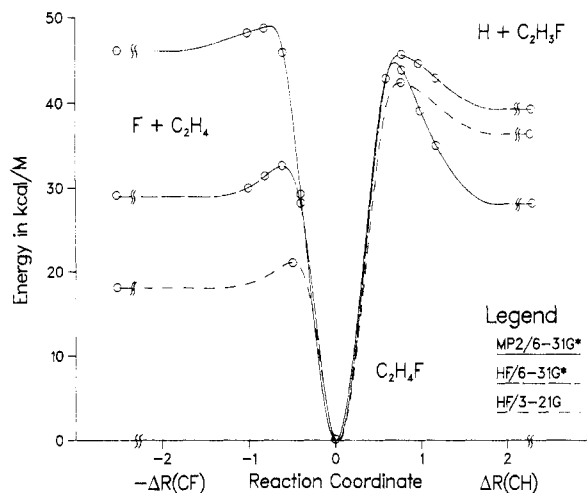


Figure 1. Comparison of calculations on the fluorine atom reacting with ethylene.

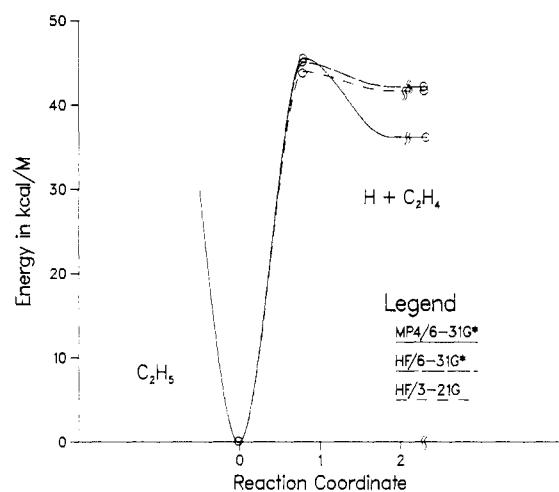


Figure 2. Comparison of calculations on the hydrogen atom reacting with ethylene.

HF/6-31G*, and MP2/6-31G* results are also presented in Figures 1 and 2. As is quite apparent from Figure 1, the qualitative shape of the energy profile for the fluorine plus ethylene reaction is very dependent on the calculated method. The heat of reaction has the wrong sign at the Hartree-Fock level. The CH and CF dissociation energies of fluoroethyl radical change by ca. ± 10 kcal/mol when the basis set is improved (HF/3-21G to HF/6-31G*) and by ca. ± 20 kcal/mol when correlation energy is added (HF/6-31G* to MP2/6-31G*). Furthermore, the shape of the barrier for hydrogen loss is markedly different if correlation energy is included, regardless of the basis set (Table I). The hydrogen plus ethylene reaction profile, Figure 2, is less sensitive to basis set and correlation effects. However, the shape of the barrier also exhibits a change similar to $C_2H_4F \rightarrow H + C_2H_3F$ when correlation energy is added.

The large basis set and electron correlation effects suggest that good agreement may be very difficult to obtain for direct comparisons with experiment. It is currently impractical to extend the size of the basis set and to improve the estimates of correlation energy to the point where all of the relative energies are unaltered by further improvements in the calculations. However, careful comparison among related reactions can yield reliable data. Heats of reaction, dissociation energies, and barrier heights are discussed individually to assess the effects of calculational level on relative energies. The final estimates for

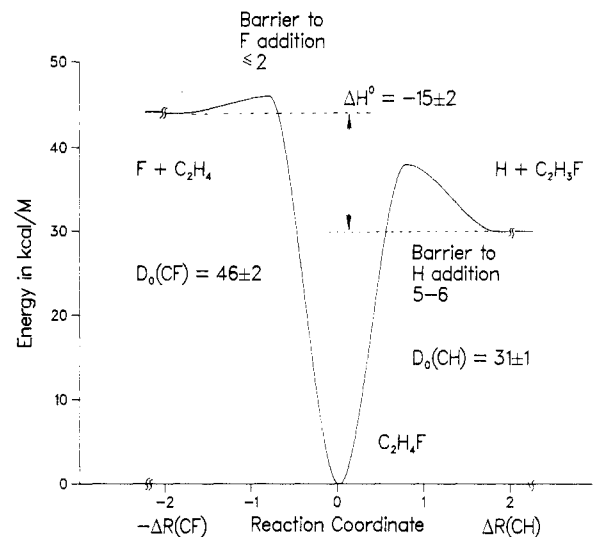


Figure 3. Best estimates for the reaction of fluorine with ethylene. The relative energies were obtained by combining experimental data with reliable theoretical energy differences and including zero-point energy.

TABLE III: Heats of Reaction^a for $F + C_2H_4 \rightarrow H + C_2H_3F$ Compared to $F + CH_4 \rightarrow CH_3F$

level	$F + C_2H_4 \rightarrow H + C_2H_3F$	$F + CH_4 \rightarrow H + CH_3F$	$CH_3F + C_2H_4 \rightarrow CH_2 + C_2H_3F$
HF/3-21G	18.34	27.48	-9.14
MP2/3-21G	-4.23	7.27	-11.50
MP3/3-21G	2.26	12.80	-10.54
MP4/3-21G	0.56	11.41	-10.85
HF/6-31G*	10.34	17.12	-6.78
MP2/6-31G*	-18.04	-8.52	-9.52
MP3/6-31G*	(-8.43)	-0.56 (-0.23)	(-8.20)
MP4/6-31G*	(-10.75)	-1.33 (-2.13)	(-8.62)
ZPE	-4.46	-3.6	-0.8
exptl	(-11 ± 2.0)	-5.6 ± 2.0	

^a Energies in kcal/mol. Estimated values in parentheses; see Methods section for description of the approximation technique.

the reaction of fluorine with ethylene are summarized in Figure 3.

Heats of Reaction. The reaction of fluorine with ethylene is thought to be exothermic by ca. 11 kcal/mol.⁴ An accurate experimental value is not available since the heat of formation of vinyl fluoride has not been measured. The value 11 ± 2 kcal/mol was obtained from Benson's additivity scheme²⁹ for C_2H_3F . Although this method can be quite reliable, there is considerable uncertainty for vinyl fluoride because of a lack of data for the =C-F group. Both the experimental and the theoretical geometries for C_2H_3F reveal that the CF and C=C bond lengths are shorter than expected,⁵ implying a special stabilization for the =C-F group not present in isolated C-F and C=C bonds. Furthermore, Lee et al. found that the angular distribution of products in their beam experiments could not be explained using 11 kcal/mol for the exothermicity.⁶ Agreement could be obtained by adopting a larger value, 14 kcal/mol.

Table III summarizes the heats of reaction for fluorine with ethylene and fluorine with methane. The 3-21G basis is inadequate, as expected from previous calculations for fluorine-containing compounds. At the MP2 level the

(29) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, 1968.

TABLE IV: Comparison of Dissociation Energies^a

level	$C_2H_4F \rightarrow F + C_2H_4$	$C_2H_4F \rightarrow H + C_2H_3F$	$C_2H_5 \rightarrow H + C_2H_4$	$C_2H_5 + C_2H_3F \rightarrow C_2H_4F + C_2H_4$
HF/3-21G	18.72	37.06	41.70	4.64
MP2/3-21G	29.86, 29.75 ^b	25.63, 25.12 ^b	32.30, 31.76 ^b	6.67, 6.64 ^b
MP3/3-21G	26.63	28.89	34.87	5.98
MP4/3-21G	27.64	28.20	34.39	6.19
CISD/3-21G			35.75	
HF/6-31G*	29.16	39.51	42.17	2.6
MP2/6-31G*	46.50	28.46	33.13	4.67
MP3/6-31G*	(41.85)	(33.42)	36.38 (37.29)	(3.87)
MP4/6-31G*	(43.37)	(32.61)	36.34 (36.76)	(4.15)
ZPE	-0.72	-5.19	-5.11	0.08
exptl			35.5 ± 1.0	

^a In kcal/mol; estimated values in parentheses. ^b Using MP2/3-21G fully optimized geometry.

heats of reaction change by 20–30 kcal/mol compared to the Hartree–Fock level. Further refinements of the estimate of correlation energy, i.e., MP3 and MP4, cause smaller but still significant changes in the heats of reaction, both with the 3-21G and the 6-31G* basis set. For $F + CH_4$, MP3/6-31G* and MP4/6-31G* calculations could be carried out directly; comparison with the estimated values indicate that the method for obtaining approximations to the MP3/6-31G* and MP4/6-31G* energies is satisfactory. At the MP4/6-31G* plus zero-point energy level, the heat of reaction of $F + CH_4$ appears to be within 1 kcal/mol of the experimental value.³⁰ A similar error can be expected for $F + C_2H_4$, suggesting ca. -15 kcal/mol for the theoretical estimate for the heat of reaction.

The difference between the two reactions, i.e., $CH_4 + C_2H_3F \rightarrow CH_3F + C_2H_4$, should be much easier to calculate. Basis set and correlation effects nearly cancel since the number of each type of bond is conserved (i.e., the difference constitutes an isodesmic reaction). The last column of Table III indicates that this is the case. A value of -9 ± 1 kcal/mol is adopted for this reaction. This, combined with the zero-point energy difference and the experimental value for $F + CH_4$, yields -15.4 ± 2 kcal/mol for the heat of reaction of $F + C_2H_4 \rightarrow C_2H_3F + H$.

Dissociation Energies. An accurate heat of formation of ethyl radical at 300 K has been obtained recently from "radical buffer" experiments.³¹ This yields $D_0 = 35.5 \pm 1.0$ kcal/mol at 0 K for ethyl radical dissociating to hydrogen and ethylene. The β -CH bond energy for the fluoroethyl radical should be similar, but the relevant experimental data are lacking. The C–F bond energy in C_2H_4F also has not been established experimentally; however, reasonable estimates for the CH bond dissociation energy and the $F + C_2H_4$ heat of reaction lead to 45–50 kcal/mol for the C–F dissociation energy of the fluoroethyl radical.

The theoretical C–F and C–H bond energies for the ethyl and fluoroethyl radicals are collected in Table IV. The unrestricted Hartree–Fock calculations for the C–H dissociation energy of ethyl radical are within 2 kcal/mol

of the experimental value when the zero-point energy difference is included. This good agreement is due to an accidental cancellation of correlation and basis set effects. Correlation energy at the MP2 level reduces the Hartree–Fock dissociation energy by ca. 9 kcal/mol (3-21G and 6-31G* bases). Higher order perturbation calculations increase the MP2 energy difference by 2–3 kcal/mol. The MP4/6-31G* plus zero-point value, 31.23 kcal/mol, is still 4 kcal/mol below the experimental dissociation energy. Part of this difference is due to the lack of p-type polarization functions on hydrogen. With a large double ζ basis set plus polarization functions on carbon and hydrogen, Harding¹³ has obtained 32.6 kcal/mol using the POL-CI method (with an enlarged active space) and correcting for zero-point energy.³² This is ca. 3 kcal/mol lower than experiment. Calculations on the dissociation energy in methane³³ and methanol³⁴ also indicate that p functions on hydrogen (e.g., 6-31G** basis set) improve the correlation energy contribution (but not the Hartree–Fock contribution) to the dissociation energy. However, there appears to be a residual error of ca. 1–2 kcal/mol not recoverable at the MP4 level with a large polarization basis set.

Similar calculational difficulties are encountered when the C–H bond dissociation energy in the fluoroethyl radical is examined. The MP2 dissociation energy differs significantly from the Hartree–Fock value; MP3 and MP4 corrections are smaller but still important. By comparison with C_2H_5 , the dissociation energy can be expected to be ca. 4 kcal/mol too low (at the (estimated) MP4/6-31G* level). The difference between the C–H bond energies in the ethyl and fluoroethyl radicals represents an isodesmic reaction and, hence, should be less sensitive to the calculational level. This difference tends toward 4.1 ± 0.5 kcal/mol. If the experimental bond dissociation energy of the ethyl radical is used and the difference in zero-point energy is taken into account, $D_0 = 31.4 \pm 1$ kcal/mol is obtained for the theoretical estimate of the β -C–H bond dissociation energy of the fluoroethyl radical.

The C–F bond energy in the fluoroethyl radical shows a large basis set effect as well as sensitivity to the method of calculating correlation energy. Unfortunately, no comparable open shell system is available for which the C–F dissociation energy is known experimentally. The C_2H_5 calculations suggest that the calculated C–F bond energy may be in error by ± 4 kcal/mol. This would lead to an

(30) The heat of formation of CH_3F , -54.88 kcal/mol at 0 K, has not been measured directly, but has been obtained by interpolation from CH_4 , CH_2F_2 , CHF_3 , and CF_4 (A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, 3, 117 (1974)). This value is probably more reliable than the heat of formation of vinyl fluoride but may also be in error.

(31) $\Delta H_{f,300}(C_2H_5) = 28.0 \pm 1.0$ kcal/mol; A. L. Castelhan, P. R. Marriott, and D. Grillier, *J. Am. Chem. Soc.*, 103, 4262 (1981). This value is supported by a thermochemical interpretation of *n*-butane pyrolysis data which yields 28.4 ± 0.5 kcal/mol; W. Tsang, *Int. J. Chem. Kinet.*, 10, 821 (1978). Taking $\Delta H_{f,298.15}(C_2H_4) = 12.496$ kcal/mol and $\Delta H_{f,300}(H)$ from the JANAF tables, and correcting for the thermal enthalpy yields $D_0 = 35.5 \pm 1$ kcal/mol.

(32) Zero-point energy differences from ref 5.

(33) R. Duchovic, H. B. Schlegel, and W. L. Hase, *Chem. Phys. Lett.*, 89, 120 (1982).

(34) G. F. Adams, G. D. Bent, G. D. Purvis, and R. J. Bartlett, *Chem. Phys. Lett.*, 81, 461 (1981).

TABLE V: Comparison of Barrier Heights

level	F + C ₂ H ₄	H + C ₂ H ₃ F	H + C ₂ H ₄	H + C ₂ H ₃ F - H + C ₂ H ₄
HF/3-21G	3.00	5.87	2.27	3.60
MP2/3-21G	4.67, 5.93 ^b	15.26, 16.23 ^b	10.88, 12.04 ^b	4.38, 4.19 ^b
MP3/3-21G	5.16	13.88	9.88	4.00
MP4/3-21G	3.26	12.99	9.09	3.90
CISD/3-21G			6.37	
UHF/6-31G*	3.59	6.20	2.90	3.30
MP2/6-31G*	0.00, 2.75 ^c	15.47, 16.30 ^c	11.80	3.67
MP3/6-31G*	(0.25), (0.60) ^c	(13.29)	10.30 (10.03)	(3.26)
MP4/6-31G*	(-2.76), (0.72) ^c	(11.85)	9.24 (8.76)	(3.09)
ZPE	-0.39	0.25	0.18	0.07
exptl			2.04 ± 0.08	

^a In kcal/mol; estimated values in parentheses. ^b Using MP2/3-21G fully optimized geometry. ^c Using MP2/31G* optimization along the HF/6-31G* reaction path.

estimated C-F bond dissociation energy of 43 ± 4 kcal/mol. An alternate value can be obtained by subtracting the estimated heat of reaction for F + C₂H₄ → C₂H₃F + H (-15 kcal/mol) from the estimated C-H bond dissociation energy in the fluoroethyl radical (31 kcal/mol) to yield a C-F bond energy of 46 ± 2 kcal/mol.

Barrier Heights. Table V compares the energies of the transition structures for the H + C₂H₄ ⇌ C₂H₅ and F + C₂H₄ → C₂H₄F → C₂H₃F + H reaction. To simplify the treatment, we will discuss the transition structures in terms of barriers for atom addition to olefins even though the C₂H₄F transition structure is reached primarily by unimolecular decomposition. As additions, the transition states occur early along the reaction path and have geometries characterized by a slightly distorted olefin with the attacking atom 1.8–2.2 Å above the carbon and making an angle of 100–110° with the C=C bond.

Experimentally the barriers to atom addition to ethylene are small. The barrier for hydrogen is 2.04 ± 0.08 kcal/mol,²⁴ while chlorine and bromine appear to have no barriers.^{10b} On this basis, the fluorine barrier is expected to be small to absent. The calculated barrier for fluorine addition is ca. 3 kcal/mol and is not very sensitive to basis set and correlation level. However, because of the large correlation contribution that increases the energy released when CF bond is formed, the position of the barrier at the MP2 level shifts to a more reactant-like geometry. If the MP2 optimized geometry is used (cf. footnote *b* and *c* in Table V), the barrier at the second-order Møller-Plesset level is 1–3 kcal/mol higher than if the Hartree-Fock geometry is used. Higher order Møller-Plesset calculations reduce the barrier by 1–2 kcal/mol and zero-point energy contributes -0.4 kcal/mol. On the basis of these trends, the actual barrier is estimated to be less than 2 kcal/mol.

Hydrogen additions to ethylene and to fluoroethylene show low barriers at the UHF level with both the 3-21G and the 6-31G* basis sets, in good agreement with experiment. However, this appears to be fortuitous. The addition of correlation energy at the MP2 level (3-21G or 6-31G* basis) increases the barrier height by 8–9 kcal/mol. Higher order contributions to the Møller-Plesset correlation energy reduce the barrier by 1–2 kcal/mol. Configuration interaction (CISD/3-21G) yields a barrier of 6.37 kcal/mol. Harding¹³ has carried out calculations with the POL-CI method, using a larger basis set than the present work and including extensive configuration interaction based on a GVB wave function. A lower barrier height is obtained (3.7 kcal/mol) which is in better agreement with experiment. The factors influencing the barrier height are being examined further, but it appears that polarization functions on hydrogen and singly excited configurations may be important.

The barrier for hydrogen addition to fluoroethylene shows the same behavior as H addition to ethylene (i.e., low barriers at the UHF level, high barrier at MP2, MP3, and MP4). On the basis of the difficulties in calculating the H + C₂H₄ barrier, the direct computation of an accurate barrier for H adding to fluoroethylene is not practical. Nevertheless, reliable information can be obtained by comparing the calculated barriers. The last column in Table V indicates that the difference in barriers for ethylene and fluoroethylene is relatively independent of basis set size and correlation method. If this difference, 3.5 ± 0.5 kcal/mol, is combined with the experimental barrier for H + C₂H₄ (2 kcal/mol) a value of 5–6 kcal/mol is predicted for H + C₂H₃F in accord with experimental estimates.⁴

Summary of Energetics. The "best estimates" for the relative energies in the F + C₂H₄ → C₂H₄F → C₂H₃F + H reaction are collected in Figure 3. The heat of reaction, -15 ± 2 kcal/mol, is obtained from a calculated difference of 9.8 kcal/mol between F + C₂H₄ → C₂H₃F + H and F + CH₄ → CH₃F + H. The experimental Δ*H*^o for the latter is -5.6 kcal/mol. The *D*₀(CH) for the fluoroethyl radical is based on the experimental *D*₀(CH) for the ethyl radical, 35.5 kcal/mol, and the calculated difference in *D*₀(CH) of -4.1 ± 0.5 kcal/mol. The *D*₀(CF) is computed from the estimated Δ*H*^o and *D*₀(CH). The barrier to F addition was calculated directly. The H addition barrier of 5–6 kcal/mol is determined by adding the calculated difference, 3.5 ± 0.5 kcal/mol, to the experimental barrier in H + C₂H₄.

Dynamical Implications

The energetics found in the present work (Figure 3) are nearly the same as those for the potential energy surface for the F + C₂H₄ → C₂H₄F → H + C₂H₃F system used by Hase and Bhalla in their trajectory study.²² Minor differences exist for the F + C₂H₄ → C₂H₄F and H + C₂H₃F → C₂H₄F exothermicities, where the F classical values obtained here are 47 ± 2 and 36.5 ± 1 kcal/mol as compared to the values of 50 and 39 kcal/mol used by Hase and Bhalla. If the trajectory results are scaled to match the energetics of Figure 3, the same value for the average fraction of available energy partitioned to H + C₂H₃F relative translation is found as reported previously, i.e., ⟨*f*_{rel}⟩ = 0.32 ± 0.03. Also from part 1 it is seen that the equilibrium and transition-state structures are nearly the same as those for the Hase-Bhalla potential energy surface.³⁵

(35) Structures for stationary points are the same for the Hase-Bhalla potential energy surface and the surface of part I in that moments of inertia are nearly identical and if the same force field is used for each surface nearly the same set of vibrational frequencies are obtained.

The major difference between the two potential energy surfaces is in the vibrational frequencies for the $F + C_2H_4$ and $H + C_2H_3F$ transition states. In particular the bending frequencies associated with rupturing C-H and C-F bends appear to be 1.5-2 times too low on the Hase-Bhalla surface. This will have a major effect on the shape of the potential energy surface in the entrance and exit channels.

The higher frequencies for the C-F bends in the entrance channel should affect the initial impact parameters and reagent orientations which lead to C_2H_4F formation, and, thus, the angular momentum distribution on C_2H_4F . Since this angular momentum goes almost exclusively to rotational energy in the C_2H_3F product,²² the vibrational frequencies in the $F + C_2H_4$ entrance channel influence the product energy distributions.

Arguments have been made that vibrational adiabaticity is important in $C_2H_4F \rightarrow H + C_2H_3F$ dissociation.^{17,18} Vibrational adiabaticity predicts that, the slower the attenuation of the bending frequencies associated with C-H rupture, the larger the relative translational energy in the

products. These bending frequencies change more rapidly for the Hase-Bhalla surface than for the surface calculated here. Thus, if vibrational adiabaticity does occur in C_2H_4F dissociation, trajectories on a potential surface adjusted to match the present ab initio results would give larger relative translational energies and a better match with experiment^{4,6} than found by Hase and Bhalla. Classical trajectory calculations to test this hypothesis are planned for the near future.³⁶

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Electron Spin Resonance and Optical Studies on Homo and Hetero Dimers of Copper(II) and Silver(II) Porphyrins

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Copper(II) and silver(II) mesoporphyrin IX dimethyl ester ($Cu^{II}MPD$ and $Ag^{II}MPD$) in tetrachloroethane (TCE) solutions exhibit at 77 K triplet ESR spectra ascribed to the homo dimers in addition to the spectra of the monomers. The optical absorption spectra of each solution show at 77 K two bands in the Soret region; one is attributed to the monomer and the other at shorter wavelengths to the homo dimer. On the other hand, an equimolar solution of the two solutes shows ESR and optical absorption spectra indicating the formation of a hetero dimer of $Cu^{II}MPD$ and $Ag^{II}MPD$ with a marked decrease in the homo dimer formation. The ESR and optical results are interpreted in terms of a structure with a face-to-face axial symmetry common to both the homo and hetero dimers. The face-to-face distances evaluated from the observed fine-structure constants are in good accord with the optical absorption data which are another measure of the separation between the two porphyrin planes of the dimers.

Introduction

Dimers and higher aggregates of metalloporphyrins in solution have been subject to increasing investigation because of their biological activities and their potential use as catalysts for multielectron redox reactions. Although a variety of spectroscopic methods have been applied to the studies of associated metalloporphyrins,¹ it is not an easy task to distinguish between dimers and higher aggregates and to elucidate geometric and electronic structures of associated species. It is, however, fairly easy to investigate the aggregated species when metalloporphyrins with a single unpaired electron are used. The spin state of the dimeric species of such metalloporphyrins becomes either singlet or triplet and accordingly their ESR spectra show only a decrease in intensity of doublet signals or an appearance of triplet signals. When higher aggregates are formed, they show exchange-broadened or exchange-narrowed ESR signals which are easily differentiated from

those of monomeric species. Thus, the distinction among monomers, dimers, and higher aggregates can be made by the ESR technique with ease. Moreover, when triplet ESR spectra are observed, their analysis leads to the elucidation of the structures of dimeric species. Triplet dimer formation has been so far reported for copper(II)²⁻⁴ and vanadyl porphyrins⁵ in frozen solutions. The solvents used for these experiments, however, freeze to a polycrystalline mass at low temperatures. Such solvents prevent measurements of optical spectra which give more information on the magnitude of the interaction between the monomer units in the dimers. Therefore, use of glass-forming solvents is desirable to obtain both optical and ESR spectra of the associated species at low temperatures.⁶

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