TABLE I: Total Energies and Vibrational Frequencies

	reactants and products		radical intermediates			transition structures		
	C_2H_4	C_2H_3F	C_2H_5	C_2H_4F (gauche)	C_2H_4F (anti)	$H + C_2H_4$	$H + C_2H_3F$	$F + C_2H_4$
				Energies[a]				
HF/3-21G	−77.60099	−175.92057	−78.16365	−176.47583	−178.47480	−78.09357	−176.40741	−176.44122
MP2/3-21G	−77.78452	−176.22087	−78.33133	−176.75710	−176.75609	−78.26153	−176.69120	−176.70024
HF/6-31G*	−78.03172	−176.88195	−78.59715	−177.44315	−177.44282	−78.52532	−177.37031	−177.39095
ZPE	34.6	30.1	39.7	35.3	35.6	34.8	30.4	34.2
				Vibrational Frequencies[b,c]				
	944 (826)	517 (490)	136	145	6i a″	614i a′	902i	428i a′
	1115 (949)	803 (713)	445 (540)	415 (425)	389 a′	415 a′	461	242 a′
	1157 (943)	1036 (923)	894	445	641 a′	448 a″	495	405 a″
	1165 (1073)	1097 (863)	1047 (1175)	931	883 a″	922 a″	552	883 a′
	1387 (1220)	1138 (929)	1111 (1138)	1055	1053 a′	976 a′	688	907 a″
	1522 (1342)	1279 (1157)	1319	1140	1107 a′	1054 a″	912	1014 a″
	1640 (1444)	1483 (1305)	1575 (1366)	1202	1281 a″	1061 a′	1006	1024 a′
	1842 (1630)	1591 (1380)	1597	1357	1427 a″	1332 a′	1074	1291 a′
	3305 (3021)	1887 (1656)	1660 (1440)	1552	1537 a′	1368 a″	1255	1367 a″
	3238 (3026)	3358 (3052)	1665 (1440)	1573	1605 a′	1625 a′	1375	1624 a′
	3371 (3103)	3419 (3080)	3149 (2842)	1684	1699 a′	1690 a′	1558	1679 a′
	3404 (3105)	3451 (3115)	3220 (2920)	3192 (2852)	3254 a′	3308 a′	1658	3315 a′
			3253 (2987)	3240	3293 a′	3320 a′	3346	3336 a′
			3291 (3033)	3319	3306 a′	3381 a″	3409	3397 a″
			3395 (3112)	3437	3414 a″	3411 a″	3447	3429 a″

[a] Total energies in atomic units (1 au = 627.51 kcal/mol); zero point energy (ZPE) in kcal/mol. For hydrogen atom HF/3-21G = −0.49620 and HF/6-31G* = −0.49823 au. For fluorine atom, HF/3-21G = −98.84501; MP2/3-21G = −98.92514; HF/6-31G* = −99.36496 au. [b] Frequencies in cm⁻¹; experimental values in parentheses: C_2H_4 from ref 24, C_2H_3F from ref 25, C_2H_5 from ref 27, and C_2H_4F from ref 28; symmetries of vibrations are indicated for C_S symmetry molecules where no experimental data are available. [c] To compare with the observed anharmonic frequencies, multiply the theoretical anharmonic frequencies by 0.89 to take into account (empirically) anharmonicity and correlation effects.

exothermic reactions. The carbon–carbon double bond is only slightly elongated and the distortion from planarity is relatively small. The attacking atom is at a distance of ca. 2 Å from the carbon and makes an angle of ca. 105° with the double bond. In each case and at all calculational levels the carbon being attacked pyramidalizes away from the approaching atom while the other carbon pyramidalizes toward the incoming atom.

The SCF optimizations (HF/3-21G and HF/6-31G*) show that the transition structure for F attacking C_2H_4 is more advanced than for H addition, as can be seen from the longer C–C bond and larger H_2CC out-of-plane angle in the C_2H_4F transition structure. This is probably an artifact of the SCF level of calculation since the exothermicity of the F + C_2H_4 reaction is drastically underestimated and the H + C_2H_4 heat of reaction is somewhat overestimated.[29] When correlation energy is added, the exothermicity of the F + C_2H_4 reaction increases and the C_2H_4F transition state becomes more reactant-like and resembles the H + C_2H_4 transition structure more closely.

Comparison of hydrogen plus ethylene with hydrogen plus fluoroethylene transition structures allows the effect of the substituents on the olefin to be examined. The H + C_2H_3F reaction is less exothermic by ca. 4 kcal/mol and the transition structure occurs slightly further along the reaction path, as gauged by the C–H* distance and then H_2CC out-of-plane angles.[45] In almost all other respects, the transition structures are very similar.

Vibrational Frequencies. Table I summarizes the vibrational frequencies for ethylene, fluoroethylene, ethyl radical, fluoroethyl radical, and the three transition structures, as calculated at the HF/3-21G level. The frequencies calculated with the 3-21G basis set agree within

±20 cm⁻¹ with those calculated at the 4-31G level.[12,18,27] The one exception[12] is the torsional mode of anti C_2H_4F. In the present calculations, this frequency is imaginary, indicating that the structure is a local maximum with respect to rotation.

On average, the harmonic frequencies calculated at the HF/3-21G level[46] are ∼11% higher than experimental values due to a combination of electron correlation and vibrational anharmonicity effects.[34,47] In a comparison of nearly 500 frequencies[46] in the range from 100 to 4000 cm⁻¹, multiplying by a scale factor (0.8 for HF/3-21G frequencies) was found to be more effective in improving the agreement with experiment than lowering the frequencies by a constant amount. The difference in the two schemes is particularly important for low-frequency modes, where subtracting a constant value can lead to anomalously low frequencies.

Experimentally, both ethyl[27] and fluoroethyl[28] radicals are characterized by a low-frequency CH stretch arising from the hydrogens β to the radical center. The theoretical calculations reproduce this shift in the frequency for ethyl radical and gauche fluoroethyl radical. Its absence in the calculated spectrum for trans fluoroethyl radical supports the assertion that the trans conformer is not the dominant structure experimentally. The electronic factors that give rise to the lengthening of the CH bond anti periplanar to the radical are also associated with a reduction in the stretching force constant for the CH bond. A similar effect is found both experimentally[48,49] and theoretically[50] for CH

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(45) The same conclusion can be reached by using the correct comparison of the C–C distances, i.e., the R(CC) in the fluoroethylene transition state relative to fluoroethylene is ca. 0.01 Å greater than the same difference for ethylene.

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bonds oriented anti to lone pairs on adjacent heteroatoms. In heterocyclic chemistry, these diagnostic low-frequency CH stretching modes are known as the Bohlmann bands.[51]

In the $F + C_2H_4$ transition structure, the normal coordinate for the imaginary frequency (i.e., the transition vector) is predominantly the CF stretch with a small portion of H_1CH_2 out-of-plane bend. The 242- and 405-cm^{-1} vibrations represent the bend of the CF in the plane and perpendicular to the FCC plane, respectively. Such frequencies are characteristic of a "tight" transition state. Since the entrance barrier is reduced slightly and shifted to a more reactant-like geometry when correlation is added (see above), these frequencies can be expected to become somewhat smaller. The other frequencies lie either between or slightly lower than the corresponding frequencies in C_2H_4 and C_2H_3F.

As expected, the vibrational structure of the $H + C_2H_4$ and $H + C_2H_3F$ transition states are very similar. The CH* bending frequencies 415, 448 cm^{-1} for $H + C_2H_4$ and 461, 552 cm^{-1} for $H + C_2H_3F$ also correspond to "tight" transition states. The lower frequencies for the former agree with the fact that the $H + C_2H_4$ is somewhat more exothermic and the transition structure occurs earlier along the reaction path. A RRKM treatment of the $H + C_2H_4$ $\rightleftharpoons C_2H_5$ reactions, using the present structural and vibrational information for the transition state along with a recent revision of the ethyl radical heat of formation, has resolved a longstanding controversy concerning the theoretical treatment of the rates for the forward and reverse reactions.[52]

The calculated vibrational frequencies of the various structures provide estimates of the change in the zero-point vibration along the reaction path (see Table I). Although the zero-point energy (ZPE) is large, the change amounts to only a few kcal/mol. Adding the fluorine increases the ZPE by less than 1 kcal/mol, since the formation of the CF bond is accompanied by the conversion of the CC double bond to a single bond. The loss of a CH bond in

going from the radical to the products results in a net decrease of 5.2 kcal/mol in the ZPE. Since the two transition states resemble the reactants (products) more than the radical, the ZPE is closer to the reactants (products); hence the entrance and exit channel barriers are not strongly affected by ZPE corrections.

Summary

In this paper we have obtained three uniform sets of geometries for the minima and saddle points for the reactions: $H + C_2H_4 \rightleftharpoons C_2H_5$ and $F + C_2H_4 \rightarrow C_2H_4F \rightarrow H + C_2H_3F$. The structures were optimized at HF/3-21G, HF/6-31G*, and MP2/3-21G levels, in order to determine the effects of polarization functions and electron correlation on the geometry. Except for the CF bonds, only small differences were found between the HF/3-21G and HF/6-31G* optimized structures. The addition of correlation energy increases bond lengths in a systematic manner but does not affect bond angles significantly. In the transition structures, the distance between the attacking (or leaving) atom change by ca. ±0.1 Å, depending on the effect of electron correlation on the energy difference in the reaction step.

Contrary to previous calculations,[12] but in agreement with ESR spectra, β-fluoroethyl radical is found to have a gauche conformation. For both the ethyl and the fluoroethyl radical, the present computations also indicate that the CH bond anti periplanar to the radical center is elongated. The associated CH stretching modes are shifted downward in frequency and correspond to the observed low-frequency CH stretching bands that are diagnostic of these radicals. The three transition structures are found to have quite similar, reactant-like geometries; however, the bending frequencies for the attacking atom are characteristic of tight transition structures.

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