Unimolecular Rate Constants, Kinetic Isotope Effects and Threshold Energies for FH and FD Elimination from CF_3CHFCH_3 and CF_3CHFCD_3

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The combination of CF_3CHF and CH_3 or CD_3 radicals was used to prepare vibrationally excited CF_3CHFCH_3 or CF_3CHFCD_3 molecules with 97 kcal mol^{-1} of internal energy. The experimental unimolecular rate constants were 3.7×10^6 s^{-1} for 2,3-FH elimination from CF_3CHFCH_3 and 1.3×10^6 s^{-1} for 2,3-DF elimination from CF_3CHFCD_3. Unimolecular rate constants for 1,2-FH elimination reaction were approximately 230 and 98 times smaller for CF_3CHFCH_3 and CF_3CHFCD_3, respectively, than the corresponding rate constants for 2,3-FH elimination. Density functional theory (DFT) was used to calculate the structures and vibrational frequencies of the molecules and transition states; this information was subsequently employed for calculations of RRKM rate constants. Comparison of the experimental and calculated rate constants gave a threshold energy of 73 ± 2 kcal mol^{-1} for the 1,2-FH elimination process and 60.5 ± 1.5 kcal mol^{-1} for the 2,3-FH elimination reaction from CF_3CHFCH_3. The calculated kinetic-isotope effects agree with the experimental results. The experimentally derived threshold energies for 1,2-FH and 2,3-FH elimination reactions from several fluoropropanes and fluorochloropropanes are summarized and compared to those from DFT calculations.

1. Introduction

Our laboratory has studied the unimolecular reactions of a series of halopropanes with the general formula CF_3CXYCH_3, where X and Y are F, Cl, or H, using the chemical activation method.[1−6] The present report, which describes the $CF_3CHFCH_3(CD_3)$ system, completes the series. The molecules were generated with 97 kcal mol^{-1} of vibrational energy by the recombination of CF_3CHF and $CH_3(CD_3)$ radicals at room temperature. These radicals were obtained by photolysis of CF_3CHFI and $CH_3I(CD_3I)$. Both 2,3-FH and 1,2-FH elimination were observed, but 2,3-FH elimination is dominant because of the lower threshold energy, E_0, with the F atom in the secondary position.

$$CF_3CHFCH_3^* \xrightarrow{k_{2,3\text{-FH}}} CF_3CH{=}CH_2 + HF \qquad (1a)$$

$$\xrightarrow{k_{1,2\text{-FH}}} CF_2{=}CFCH_3 + HF \qquad (1b)$$

$$+ M \xrightarrow{k_M} CF_3CHFCH_3 + M \qquad (1c)$$

The bath gases, M, are CH_3I (CD_3I) and CF_3CHFI in these experiments. Collisional deactivation, reaction 1c, should be efficient for these molecules, and the usual unit deactivation assumption gives the experimental rate constants as $k_{2,3-FH} = k_M[M]([CF_3CH{=}CH_2]/[CF_3CHFCH_3])$ and $k_{1,2-FH} = k_M[M]([CF_2{=}CFCH_3]/[CF_3CHFCH_3])$. The products from the decomposition reactions, $CF_3CH{=}CH_2$ and $CF_2{=}CFCH_3$, are labeled as D_i and S represents the CF_3CHFCH_3 product stabilized by collision. The $1/[M] = 1/P$, so that a plot of D/S versus inverse pressure can be used to the determine the experimental $k_{2,3-FH}$ rate constant. The $k_{2,3-FH}/k_{1,2-FH} = [CF_3CH{=}CH_2]/[CF_2{=}CFCH_3]$ and, if the rate constants differ by more than a factor of 10, this product ratio is the most convenient and reliable method for determining the rate constant for the slower reaction.

Experiments also were done with CF_3CHFCD_3 to measure the kinetic isotope effects for reactions 1a and 1b. These unimolecular rate constants can be assigned to a specific vibrational energy, which is given by the average internal energy of the molecule formed by radical recombination.

In recent work[4−6] we have employed electronic structure calculations using density functional theory (DFT) at the B3PW91 level with the 6-31G(d′,p′) basis set to assign structures and vibrational frequencies to haloethane and halopropane molecules and their transition states for HF and HCl elimination. These properties of the transition states are not very sensitive to the level of theory or the basis sets,[4−9] especially for HF elimination, and the calculated frequencies of the transition states should be reliable. These calculated frequencies and moments of inertia subsequently are used with statistical (RRKM) unimolecular rate theory to calculate rate constants at a given energy. In the rate constant calculations, the torsionsal motions of the CH_3 and CF_3 groups were treated as hindered internal rotors.[4] The threshold energy, E_0, is treated as a parameter to be obtained by matching the calculated rate constant, k_E, to the experimental rate constant. The E_0 values assigned by this procedure were shown to agree with threshold energies obtained by thermal activation experiments for several test cases.[4] Using this approach, the experimental data to be reported in this study enable E_0 to be assigned for 1,2-FH and 2,3-FH elimination from CF_3CHFCH_3. The data for CF_3CHFCD_3 provide a consistency test for the computations and for the experimental measurements. The uncertainty in the E_0 values assigned from fitting experimental rate constants measured at a single energy will be discussed for the 2,3-FH and 2,3-FD elimination reactions.

The assignment of E_0 for 2,3-FH elimination from CF_3CHFCH_3 enables a comparison to be made with $CF_3CF_2CH_3$ and $CF_3CFClCH_3$,[6] which illustrates the effects of F and Cl

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substituents in the secondary position on threshold energies. Comparison can be made for 1,2-FH loss for the $CF_3CH_2CH_3$, CF_3CHFCH_3 and CF_3CHFCF_3 series and for 2,3-FH loss from CF_3CHFCH_3 and CH_3CHFCH_3 to illustrate the effect of CH_3 and CF_3 groups on threshold energies. Finally, comparison can be made with CF_3CHFCH_3 vs CH_3CH_2F and CF_3CH_2F to see the effects upon E_0 for adding a CF_3 group or a CH_3 group to the ethanes. Several comparisons also are possible with molecules such as $CF_2ClCF_2CH_3$. These experimentally assigned threshold energies also are compared to values from DFT calculations.

Two additional motivations for investigating CF_3CHFCH_3 are as follows: (1) By comparison to the E_0's for CF_3CH_3 (69 kcal mol^{-1})[4,7] and CFH_2CH_3 (58 kcal mol^{-1}),[4] the E_0 for 1,2-FH and 2,3-FH elimination from CF_3CHFCH_3 are anticipated to differ by about 10 kcal mol^{-1} and the computed structure of the two transition states might provide some insight into reasons for this difference. (2) We have reported a novel ClF interchange reaction for $CF_2ClCF_2CH_3$[3] and CHF_2CH_2Cl.[8a] We are completing work for $CF_2ClCHFCH_3$ and $CF_2ClCHFCD_3$[8b] in which 2,3-FH elimination, the dominant pathway, and 1,2-HCl loss, the slowest channel, are competitive with the 1,2-ClF interchange reaction. The development of a reliable method for assigning threshold energies for the HF elimination reactions for CF_3CHFCH_3 and HCl for other chlorofluoroalkanes should facilitate utilization of the same methodology for determining threshold energies for FCl interchange in $CF_2ClCHFCH_3$ and similar halopropanes.

2. Experimental Methods

Pyrex vessels with volumes ranging from 15 to 3500 mL containing 0.14 μmol of 1-iodo-1,2,2,2-tetrafluoroethane and 2.1 μmol of iodomethane-d_0 or iodomethane-d_3 and small amounts of mercury(I) iodide were photolyzed with an Oriel high-pressure 250 W mercury lamp. The presence of mercury(I) iodide in the vessels during photolysis aids in formation of the methyl and 1,2,2,2-tetrafluoroethyl radicals.[1−5] Photolyses were done at room temperature with irradiation periods between 30 s and 4 min; the longer irradiation times correspond to vessels with larger volume. The typical percentage conversion for experiments from which decomposition and stabilization ratios were measured were less than 5% for the iodomethane and about 30% for the 1-iodo-1,2,2,2-tetrafluoroethane. Longer photolysis times were used to obtain sufficient material for mass spectrometric analysis. Sample preparation was done on a grease-free vacuum line, and pressures of all gases were measured with a MKS 270 electronic manometer. The CH_3I was purchased from Aldrich, and the CF_3CFHI was purchased from PCR (now SynQuest).

Product identification was based on mass spectral fragmentation patterns and gas chromatographic retention times. A Shimadzu QP 5000 GC−MS with 0.25 mm by 105 m Rtx-200 column was used for mass analysis. Table 1 shows the mass spectral patterns for the products of interest; a commercial sample was available for only $CF_3CH{=}CH_2$. To determine the GC retention time and mass spectrum of $CF_2{=}CFCH_3$ an authenic sample was prepared by the elimination of HCl from chemically activated $CF_2ClCHFCH_3$ that was formed by the photolysis of $CF_2ClCHFI$ and methyl iodide. Assignment of the *meso*- and *d*,*l*-diastereometers for $CF_3CHFCHFCH_3$ was based upon the retention time for the *meso*- and *d*,*l*-diastereomers for $CF_3CH_2CHClCHClCH_2CF_3$. Data for determination of rate constants were collected using a 0.53 mm × 210 m Rtx-200 combination column in a Shimadzu GC-14A with flame ionization detector and a Shimadzu CR501 Chromatopac Integrator for measurement of peak areas. A block of dry ice was added to the GC oven to achieve subambient temperatures, which improved separation of the earliest eluted components. After 12 min, the temperature of the GC column was raised to 50 °C. Typical retention times were as follows: C_2H_6, 10 min; $CF_3CH{=}CH_2$, 11 min; $CF_2{=}CFCH_3$, 11.5 min; CF_3CHFCH_3, 12 min; *meso*- and *d*,*l*-$CF_3CHFCHFCF_3$, 13 and 15 min; CH_3I, 20 min; and CF_3CHFI, 21 min. Since sufficient quantities of CF_3CHFCH_3 and $CF_2{=}CFCH_3$ were not available, the calibration factors for the flame ionization detection for $[CF_3CH{=}CH_2]/[CF_3CHFCH_3]$, $[CF_3CH{=}CH_2]/[CF_2{=}CFCH_3]$ and the deuterated analogues were assumed to be 1.0. This is consistent with FID calibration factors from previous work from this laboratory[1,2,4] for cases in which the fluoroalkene and fluoroalkane molecules were not completely fluorinated. This assumption could introduce a 5−10% systematic uncertainty in the product ratios and, hence, the rate constants.

TABLE 1: Mass-Spectral Fragmentation Data at 70 eV (*m*/*e*, Relative Abundance and Assignment)

$CF_3CH{=}CH_2$			$CF_3CH{=}CD_2$		
m/*e*	RA	assignment	*m*/*e*	RA	assignment
95	100	$C_3F_3H_2^+$	98	100	$C_3F_3HD_2^+$
96	82	$C_3F_3H_3^+$	79	93	$C_3F_2HD_2^+$
77	80	$C_3F_2H_3^+$	96	80	$C_3F_3HD^+$
69	46	CF_3^+	97	55	$C_3F_3D_2^+$
51	35	CF_2H^+	69	47	CF_3^+
75	24	$C_3F_2H^+$	51	43	CF_2H^+
$CF_2{=}CFCH_3$			$CF_2{=}CFCD_3$		
m/*e*	RA	assignment	*m*/*e*	RA	assignment
96	100	$C_3F_3H_3^+$	99	100	$C_3F_3D_3^+$
95	99	$C_3F_3H_2^+$	97	81	$C_3F_3D_2^+$
69	97	CF_3^+	69	80	CF_3^+
51	74	CF_2H^+	52	76	CF_2D^+
46	58	$C_2FH_3^+$	49	63	$C_2FD_3^+$
75	34	$C_3F_2H^+$	31	32	CF^+
CF_3CHFCH_3			CF_3CHFCD_3		
m/*e*	RA	assignment	*m*/*e*	RA	assignment
47	100	$C_2FH_4^+$	50	100	CF_2^+, $C_2FHD_3^+$
69	44	CF_3^+	69	26	CF_3^+
77	40	$C_3F_2H_3^+$	79	12	$C_3F_2HD_2^+$
51	25	CF_2H^+	51	12	CF_2H^+
27	23	$C_2H_3^+$	100	11	$C_3F_3HD_3^+$
97	11	$C_3F_3H_4^+$	80	8	$C_3F_2D_3^+$
meso-$CF_3CHFCHFCF_3$			*d*,*l*-$CF_3CHFCHFCF_3$		
m/*e*	RA	assignment	*m*/*e*	RA	assignment
69	100	CF_3^+	69	100	CF_3^+
113	40	$C_3F_4H^+$	113	35	$C_3F_4H^+$
51	30	CF_2H^+	51	34	CF_2H^+
95	28	$C_3F_3H_2^+$	95	27	$C_3F_3H_2^+$
114	24	$C_3F_4H_2^+$	133	18	$C_3F_5H_2^+$
101	12	$C_2F_4H^+$	114	17	$C_3F_4H_2^+$
82	11	$C_2F_3H^+$	101	14	$C_2F_4H^+$
133	9	$C_3F_5H_2^+$	82	13	$C_2F_3H^+$

3. Results

3.1. Experimental Rate Constants. The rate for 1,2-FH elimination is much slower than for 2,3-FH elimination, and the yield of $CF_2{=}CFCH_3$ was too small to be measured accurately in the pressure range needed to measure the *D*/*S* ratio to establish the rate constant for 2,3-FH elimination. Therefore, experiments first were done over the pressure range from 2.8 to 0.08 Torr to measure the ratios of $CF_3CF{=}CH_2/CF_3CHFCH_3$

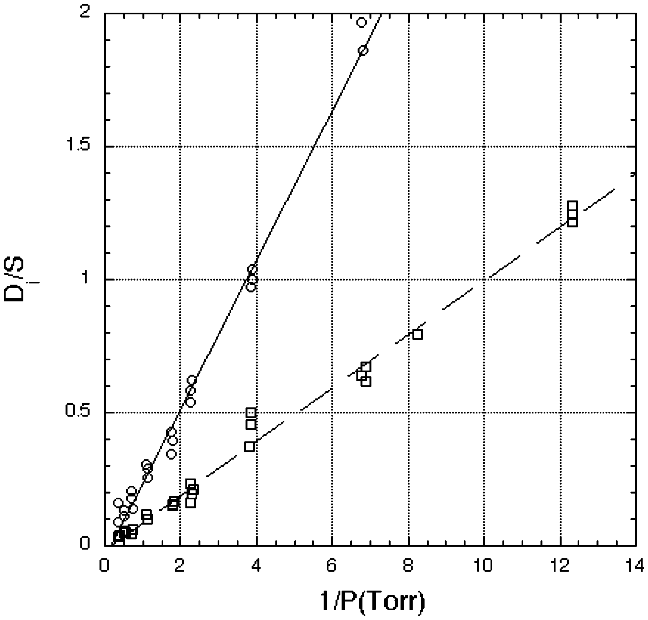

Figure 1. Plot of $CF_3CH{=}CH_2/CF_3CHFCH_3$ (○) and $CF_3CH{=}CD_2/CF_3CHFCD_3$ (□) vs inverse pressure. The slope and intercept values are 0.280 ± 0.006 and -0.04 ± 0.02 for CF_3CHFCH_3 and 0.101 ± 0.002 and -0.01 ± 0.01 for CF_3CHFCD_3.

and $CF_3CF{=}CD_2/CF_3CHFCD_3$ from reaction 1a. A second set of experiments at lower pressure was done to measure the $CF_2{=}CFCH_3/CF_3CH{=}CH_2$ and $CF_2{=}CFCD_3/CF_3CF{=}CD_2$ ratios. The *D*/*S* versus 1/*P* plots for 2,3-FH and 2,3-FD elimination from CF_3CHFCH_3 and CF_3CHFCD_3, respectively, are shown in Figure 1. The slopes are 0.280 ± 0.006 Torr for the 2,3-FH reaction and 0.101 ± 0.002 Torr for the 2,3-DF pathway. The high-pressure intercepts are -0.040 and -0.0091 for the CF_3CHFCH_3 and CF_3CHFCD_3 plots, respectively, and the correlation coefficient is 0.995 for both data sets. These intercepts should be, and are, effectively zero, and these data appear to be a reliable measure of the limiting high-pressure rate constants. These data give a kinetic-isotope effect of 2.8 ± 0.1 for 2,3-FH vs 2,3-DF elimination.

For pressures sufficiently low that most of the CF_3CHFCH_3 decomposes, the small $CF_2{=}CFCH_3$ yield could be measured. Based on five experiments over the pressure range of 0.033−0.015 Torr the $[CF_3CH{=}CH_2]/[CF_2{=}CFCH_3]$ ratio was 230 ± 80 and the $[CF_3CH{=}CD_2]/[CF_2{=}CFCD_3]$ ratio was 98 ± 22. These product ratios are equivalent to rate constant ratios. Converting to rate constants gives $(1.2 \pm 0.4) \times 10^{-3}$ and $(1.0 \pm 0.2) \times 10^{-3}$ Torr for 1,2-FH elimination from CF_3CFHCH_3 and CF_3CFHCD_3, respectively. The large uncertainty in these rate constants is a consequence of the small yields of $CF_2{=}CHFCH_3$ and $CF_2{=}CHFCD_3$. The kinetic isotope effect for 1,2-FH elimination (1.2) is smaller than for 2,3-FH and 2,3-DF elimination (2.8), because HF elimination from CF_3CFHCD_3 does not include a primary isotope effect. Unfortunately, the experimental uncertainty of this secondary kinetic-isotope effect for reaction 1b is relatively large.

The rate constants in pressure units were converted to units of s^{-1} by multiplication by the collision rate constant $k_{A,M} = \pi d^2_{A,M}(8kT/\pi\mu_{A,M})^{1/2}\Omega^{2,2}(T^*)$. The collision diameters (and ϵ/k) values used for the calculation are 4.6 Å (405 K), 5.2 Å (300 K), and 5.6 Å (240 K) for CH_3I, CF_3CFHI, and CF_3CHFCH_3, respectively.[4] The collision diameters and the ϵ/k values used for CF_3CHFI and CF_3CHFCH_3 are the same estimates that were employed for CF_3CF_2I and $CF_3CF_2CH_3$.[6] The unimolecular rate constants are $(3.7 \pm 0.4) \times 10^6$ and $(1.3 \pm 0.2) \times 10^6$ s^{-1} for 2,3-FH (FD) elimination from CF_3CHFCH_3 and CF_3CHFCD_3, respectively. The uncertainty in the collision rate constants together with the unit deactivation assumption introduces a 10−15% uncertainty into the rate constants in s^{-1} units. This uncertainty is larger than the uncertainty of the slopes of the *D*/*S* plots, and the uncertainty in the rate constants (in s^{-1} units) is cited as ±15% for 2,3-FH and -FD elimination here and in Table 2. The rate constants for 1,2-FH elimination from CF_3CHFCH_3 is $(1.6 \pm 0.5) \times 10^4$ s^{-1} and that for 1,2-FH elimination from CF_3CHFCD_3 is $(1.3 \pm 0.3) \times 10^4$ s^{-1}; these uncertainties are the same as those for the experimental product ratios.

TABLE 2: Comparison of Experimental and Calculated Rate Constants

molecule	$\langle E\rangle^a$ (kcal mol^{-1})	rate constants, s^{-1} exptl	rate constants, s^{-1} calcd^c	$E_0{}^d$ (kcal mol^{-1})
CF_3CHFCH_3	97.0			
2,3-FH		$(3.7 \pm 0.4) \times 10^6$	3.8×10^6	60.5
1,2-FH		$(1.6 \pm 0.5) \times 10^4$	2.0×10^4	73
CF_3CHFCD_3	97.3			
2,3-FD		$(1.3 \pm 0.2) \times 10^6$	1.3×10^6	61.5
1,2-FH		$(1.3 \pm 0.3) \times 10^4$	1.3×10^4	73

[a] Average vibrational energy of the formed molecules. [b] See text for collision cross sections used to convert the rate constants in Torr units to s^{-1}. [c] Calculated from RRKM formulation of unimolecular rate constants, eq 3. [d] Assigned by matching the calculated and experimental rate constants.

3.2. Thermochemistry. The average vibrational energy of the CF_3CHFCH_3 molecules can be obtained from eq 2, assuming that the activation energy for the radical recombination reaction is negligible.

$$\langle E_V\rangle = D_0(CF_3CHF\text{-}CH_3) + 3RT + \langle E_V(CH_3)\rangle + \langle E_V(CF_3CHF)\rangle \quad (2)$$

The $\Delta H°_{f,298}$ of CH_3, CF_3CHF and CF_3CHFCH_3 were used to find $D_{298}(CF_3CHF\text{-}CH_3)$, which was adjusted to D_0. The thermal energies of the radicals can be easily estimated, and the uncertainty in $\langle E_V\rangle$ arises from lack of firm assignment for $\Delta H°_f(CF_3CHFCH_3)$ and $\Delta H°_f(CF_3CHF)$. The former has been estimated previously as −225.6 kcal mol^{-1} from utilization of an isodesmic reaction.[6] The $\Delta H°_{f,298}(CF_3CHF)$ values[10−12] range from −168 to −163 kcal mol^{-1}. Combining these numbers with the established $\Delta H°_{f,298}(CH_3)$[13] = 35.0 kcal mol^{-1}, gives $\langle E_V\rangle = 97 \pm 2$ kcal mol^{-1} as the average vibrational energy of CF_3CHFCH_3 formed by recombination of CH_3 + CF_3CFH radicals at 298 K. The $\langle E_V\rangle$ for CF_3CHFCD_3 is 0.3 kcal mol^{-1} larger than that for CF_3CHFCH_3. For our choice of thermochemistry,[6] the $\langle E_V\rangle$ of the $CF_3CFClCH_3$, CF_3CFHCH_3, and $CF_3CF_2CH_3$ molecules formed by recombination with CH_3 radicals are 94, 97, and 98 kcal mol^{-1}. The ordering for these bond dissociation energies seems reasonable, although the uncertainty in each value is ±2 kcal mol^{-1}.

3.3. Calculated Results. The theoretical formulation of statistical unimolecular rate constants,[14] RRKM theory, is used in the form of eq 3 to assign threshold energies, E_0, to reactions 1a and 1b and to their counterparts with CF_3CFHCD_3.

$$k_E = \frac{s^\ddagger}{h}\left(\frac{I^\ddagger}{I}\right)^{1/2}\frac{\Sigma P^\ddagger(E - E_0)}{N^*_E} \quad (3)$$

In eq 3 the vibrational energy, *E*, is equated to the average internal energy, $\langle E_V\rangle$, of the molecule. The sum of states,

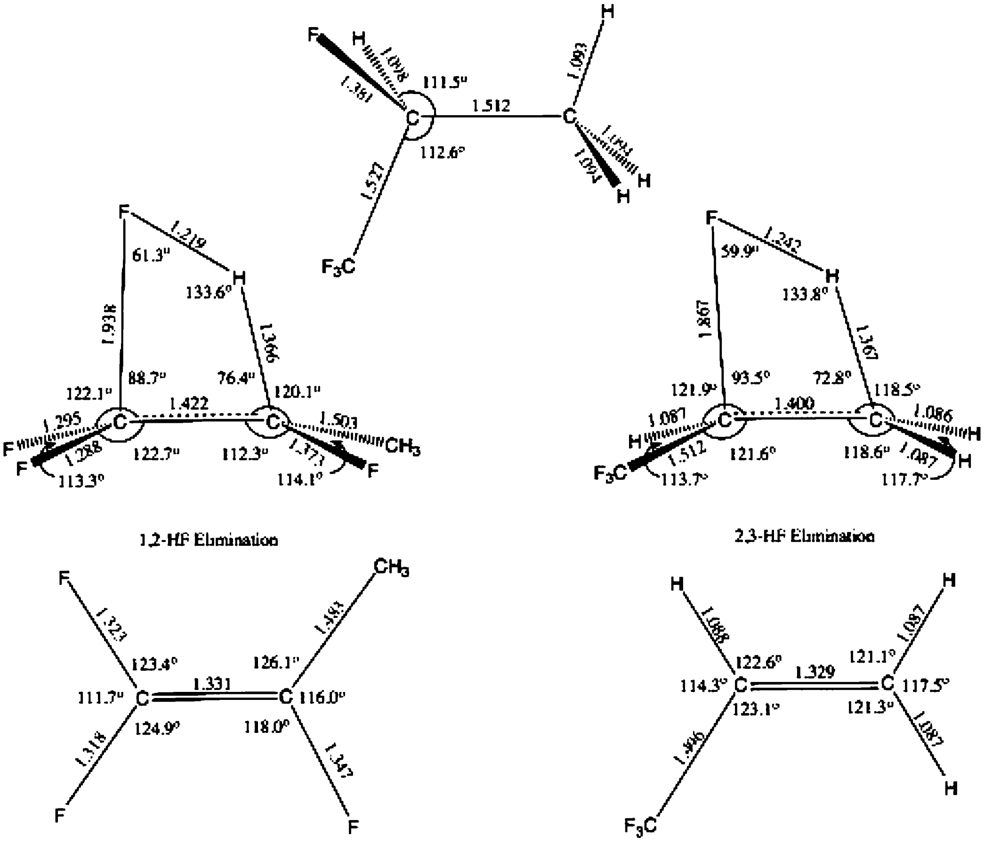

Figure 2. Computed geometries (bond distances are in Å and angles are in deg) for CF_3CHFCH_3 and for the 1,2-FH and 2,3-FH elimination transition states using DFT (B3PW91) calculations with a 6-31G(d′,p′) basis set. The C−F bond distances for the CF_3 group of CF_3CHFCH_3 are 1.34−1.35 Å. The ring dihedral angle is 1.11° and 0.618° for the 1,2-FH and 2,3-FH elimination transition states, respectively. For the 1,2-FH transition state the angle between the triangular plane of the CF_2 end and the C═C bond is 167.3° and the corresponding angle for the $CFCH_3$ end is 144.5°. The equivalent angles are 164.0° for the $CHCF_3$ end and 157.4° for the CH_2 end of the 2,3-FH elimination transition state.

$\Sigma P^{\ddagger}(E - E_0)$, of the transition state and the density of states, N^*_E, of the molecule were obtained from the Multiwell code.[15] The reaction path degeneracies, $s^{\ddagger}$, are 3 for both reactions 1a and 1b. The moments of inertia, I and $I^{\ddagger}$, and vibrational frequencies of the molecule and transition states, which are needed to calculate k_E, were obtained from the Gaussian Suite of programs.[16] We have continued[4−6] to use DFT at the B3PW91 level with the 6-31G(d′p′) basis set for computation of molecular and transition state structures. In previous publications, which summarized the unimolecular reactions of several fluoropropanes, we have demonstrated that these computations provide reliable vibrational frequencies.[4,6,8] The calculated structures and properties of the transition states and molecules are provided in Figure 2 and in Table 4. The DFT calculations, even with a more advanced level theory and larger basis sets, do not necessarily provide reliable E_0 values for FH elimination reactions,[6,8] and these are assigned by matching the calculated rate constant, $k_{\langle E\rangle}$, from eq 3 with the experimental rate constant, k(exp).

In evaluating the harmonic sums of states and densities of states, the torsional modes of the CF_3 and CH_3 groups were treated as hindered internal rotations (HIR). The reduced moments of inertia are $I_{\text{red}}(CF_3) = 35.9$ and $I_{\text{red}}(CH_3) = 3.14$ amu Å^2 with potential energy barriers[17] of $V(CF_3) = 4.9$ and $V(CH_3) = 3.3$ kcal mol^{-1} for CF_3CHFCH_3. The potential barriers were assumed to be unchanged in the transition states, but the moments of inertia were evaluated for each structure and $I^{\ddagger}_{\text{red}}(CF_3) = 39.4$ and $I^{\ddagger}_{\text{red}}(CH_3) = 3.13$ amu Å^2 for 2,3-FH and 1,2-FH elimination, respectively. The reduced moments for the CF_3CHFCD_3 system were $I_{\text{red}}(CD_3) = 6.17$, $I_{\text{red}}(CF_3) = 39.1$, $I^{\ddagger}_{\text{red}}(CD_3) = 6.16$, and $I^{\ddagger}_{\text{red}}(CF_3) = 41.4$ amu Å^2.

TABLE 3: Comparison of Calculated and Experimental E_0[a] for 2,3-FH and 1,2-FH Elimination

2,3-FH elimination			1,2-FH elimination		
molecule	exptl	calcd[b]	molecule	exptl	calcd[b]
CF_3CFHCH_3	60.5[c]	62	CF_3CHFCH_3	73[c]	74
$CF_3CF_2CH_3$	65[d]	66	$CF_3CH_2CH_3$	69[e]	69
$CF_3CFClCH_3$	61.3[d]	64	$CF_3CH_2CH_2Cl$	71[e]	67
CH_3CHFCH_3	55[e]	57	$CF_3CH_2CF_3$	73[e]	67
$CH_3CF_2CH_3$	∼55[g]	60	CF_3CHFCF_3	∼75[h]	∼72[h]
CH_2FCH_3	58[e]	59	CF_3CH_3	69[e]	69
			CF_3CH_2F	∼69[i]	

[a] In units of kcal mol^{-1}. The experimental E_0 values usually have uncertainties of ±1.5 kcal mol^{-1}. [b] Obtained from DFT (B3PW91) calculations with 6-31G(d′,p′) basis set. [c] This work. [d] Reference 6. [e] Reference 4 and see text for discussion of $CF_3CH_2CH_3$. [f] Reference 3. [g] Reference 4; the experimental E_0 value for $CH_3CF_2CH_3$ may be a lower limit. [h] Reference 5. [i] Reference 20, obtained from Arrhenius activation energies.

The calculated rate constants are shown in Figure 3 for 2,3-FH and 2,3-FD elimination reactions. Since we wish to compare threshold energies for a series of 2,3-FH and 1,2-FH elimination reactions, this figure is presented to demonstrate the dependence of the E_0 assignments on the uncertainties in k_a(exp) and $\langle E_V\rangle$ and how independent results from CF_3CHFCD_3 help better to define the threshold energy. The threshold energies for the reactions from CF_3CFHCD_3 are fixed by the zero-point energy differences relative to the threshold energies for the CF_3CHFCH_3 reactions. Thus, E_0(2,3-FH) and E_0(1,2-FH) from CF_3CHFCH_3 are the only parameters to be determined. The ratio of rate constants for reactions 1a and 1b depends on both the two threshold energies and any intrinsic difference in the sums of

TABLE 4: Computed Moments of Inertia and Vibrational Frequencies for CF_3CFHCH_3 and CF_3CFHCD_3 and the Transition States Using B3PW91/6-31G(d′,p′)

moments of inertia, amu Å^2	frequencies,^{a} cm^{-1}
CF_3CHFCH_3 143.6, 212.0, 258.4	72.9*, 208, 226*, 247, 333, 410, 474, 543, 578, 670, 806, 926, 1032, 1140, 1157, 1198, 1237, 1312, 1364, 1410, 1416, 1489, 1502, 3079, 3082, 3173, 3176
1,2-HF transition state 163.5, 236.8, 265.6	1806i, 100, 194*, 213, 262, 270, 303, 350, 495, 554, 581, 742, 802, 967, 1050, 1166, 1190, 1286, 1403, 1436, 1475, 1498, 1620, 1728, 3061, 3143, 3169
2,3-HF transition state 143.1, 225.9, 271.6	1854i, 76.4*, 174, 242, 319, 392, 506, 513, 557, 577, 641, 683, 825, 869, 1008, 1057, 1179, 1237, 1243, 1286, 1310, 1434, 1553, 1629, 3176, 3232, 3279
CF_3CHFCD_3 151.8, 225.3, 277.1	69.5*, 163*, 201, 237, 312, 403, 443, 533, 568, 624, 757, 788, 932, 996, 1065, 1072, 1127, 1176, 1195, 1232, 1314, 1365, 1417, 2215, 2351, 2355, 3080
2,3-DF transition state 150.9, 238.0, 289.0	1395i, 74.4*, 172, 225, 311, 356, 407, 500, 550, 563, 595, 629, 686, 777, 877, 938, 1018, 1036, 1172, 1190, 1224, 1294, 1317, 1514, 2311, 2444, 3233
1,2-HF transition state 172.0, 251.7, 285.8	1807i, 93.0, 143*, 203, 256, 264, 294, 331, 483, 538, 561, 720, 778, 809, 861, 1043, 1061, 1078, 1160, 1189, 1296, 1427, 1611, 1726, 2202, 2328, 2348

[a] Frequencies that were replaced by hindered internal rotors are designed with an asterisk.

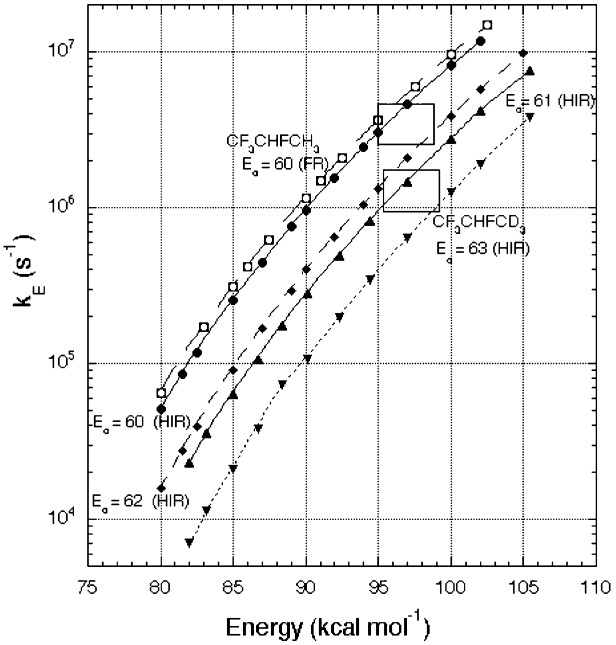

Figure 3. Plots of log k_E vs E for two E_0 values for 2,3-FH and 2,3-FD elimination from CF_3CHFCH_3 (top three curves) and CF_3CHFCD_3 (bottom two curves) for the hindered internal rotor models (HIR). The k_E for the free internal rotor model (FR) of CF_3CHFCH_3 is shown for $E_0 = 60$ kcal mol^{-1}. The ranges of uncertainty for $\langle E_V \rangle$ and k(exp) are shown by the upper and lower boxes for CF_3CHFCH_3 and CF_3CHFCD_3, respectively; the preferred value is in the center of the boxes.

states of the 1,2-FH and 2,3-FH elimination transition states. Therefore, the nature of the two transition states will be examined before the E_0 values are selected.

A global measure of the difference in transition states for 1,2-FH and 2,3-FH elimination is a comparison of their internal partition functions (q_i) and moments of inertia ($I_i^{\ddagger}$). Both are larger for the 1,2-FH elimination transition state with ratios of $(I_{1b}^{\ddagger}/I_{1a}^{\ddagger})^{1/2} = 1.08$ and $(q_{1b}/q_{1a}) = 2.0$ for vibrational models or 1.9 for HIR models; the partition functions were calculated at 800 K. The lower vibrational frequencies for the 1,2-FH elimination transition state give ratios of $\Sigma P^{\ddagger}(1b)/\Sigma P^{\ddagger}(1a) = 2.2$ and 1.9 for vibrational and HIR models at a common energy of 35 kcal mol^{-1}. This difference in transition states means that $E_0(1b) - E_0(1a)$ must be larger than it would be, if the structures of the two transition states were equivalent, to obtain a given value for $k(1a)/k(1b)$. Although the 2,3-FH transition state has a -CF_3 internal rotor while the 1,2-FH transition state has a -CH_3 internal rotor, the frequencies associated with the three out-of-ring C−F bonds of the 1,2-HF transition state are, collectively, lower than the frequencies of the CF_3 group. This difference between the 1,2 and 2,3 elimination pathways is an intrinsic property of the reactions of CF_3CXYCH_3-type molecules.

Examination of Figure 3 shows that for $\langle E_V \rangle = 97.0$ and 97.3 kcal mol^{-1}, threshold energies of 60.5 and 61.5 kcal mol^{-1} provide a satisfactory fit to the $k_{2,3-FH}$ and $k_{2,3-FD}$ of CF_3CHFCH_3 and CF_3CHFCD_3, respectively. Given the uncertainties in the experimental and calculated rate constants, exact fitting of threshold energies beyond ±0.5 kcal mol^{-1} has no physical significance. A 1 kcal mol^{-1} difference in threshold energies for $CF_3CFHCH_3(CD_3)$ is consistent with the predicted $E_0(FD) - E_0(FH)$ of 0.97 kcal mol^{-1} from zero-point energy considerations.

Inspection of the zero-point energies shows that 1,2-FH elimination from CF_3CHFCH_3 and CF_3CHFCD_3 should have nearly the same E_0 value (the difference is only 0.05 kcal mol^{-1}). Since $k_{1,2-FH}$ is thought to be more reliable from CF_3CHFCD_3, that system will be examined first. The dependence of k_E upon E_0 from 2,3-FD elimination shown in Figure 2 can be used to provide an estimate for E_0(1,2-FH). A 2 kcal mol^{-1} change in E_0 alters k_E by a factor of 2.3 at $E = 97$ kcal mol^{-1}. Thus, a 98-fold reduction in k_E requires approximately a 10 kcal mol^{-1} higher threshold energy. However, the 1,2-FH and 2,3-FD transition states differ, as mentioned above, and an even larger difference in E_0 values is needed. Fitting the ratio of rate constants gives the best measure of E_0(1b) because the properties of the molecule cancel and, only the difference in E_0(1b) and E_0(1a) matters. Fitting the ratios of rate constants for reactions 1a and 1b of 230 ± 80 and 98 ± 22 from CF_3CFHCH_3 and CF_3CFHCD_3, respectively, gave $E_0(1,2\text{-FH}) - E_0(2,3\text{-FH}) = 13.5$ kcal mol^{-1} and $E_0(1,2\text{-FH}) - E_0(2,3\text{-FD}) = 11.5$ kcal mol^{-1}. The uncertainties in the experimental product ratios give a ±1.0 kcal mol^{-1} uncertainty for the E_0(1,2-FH) assignment for each case. As an alternative method, the absolute values of the rate constants can be fitted, see Table 2. We recommend an E_0(1,2-FH) of 73 kcal mol^{-1} for CF_3CHFCH_3 or CF_3CHFCD_3.

The calculated secondary kinetic-isotope effect for 1,2-FH elimination from CF_3CHFCD_3 vs CF_3CHFCH_3 is 2.2 for a fixed common threshold energy of 73.0 kcal mol^{-1}. This value is considerably larger than the experimental value of 1.2. The latter has a large uncertainty due to the very small yields of $CF_2{=}CFCH_3$ and $CF_2{=}CFCD_3$ from reaction 1b, and the calculated ratio is preferred.

4. Discussion

4.1. Threshold Energies for CF_3CHFCH_3. The CF_3CHFCH_3 molecule is the simplest member of the series that can have competitive 2,3-FH and 1,2-FH elimination. Thus, it is important to understand the uncertainties in the assignment of the E_0 values for reaction 1. The source of the uncertainties are the experimental error in the D/S plot, the choice of collision cross sections for calculation of k_M, the uncertainty in the assignment of $\langle E_V \rangle$, possible deficiencies of the transition state, and inherent limitations of the theory behind eq 3. Several of these questions can be discussed with the aid of Figure 3.

The average energy of CF_3CHFCH_3 carries a ±2 kcal mol^{-1} uncertainty. As shown in Figure 3, a decrease in energy from 97 to 95 kcal mol^{-1} would lower k_E by a factor of 1.4−1.5. The uncertainty in a carefully measured high pressure experimental rate constant, which lies primarily in the choice of collision cross sections used to find k_M, is typically equal to or less than 30%; see Figure 1 for the uncertainty in the slopes of the *D*/*S* plots. Although the collisional efficiency of CH_3I and CF_3CFHI have not been measured, we have argued[4] that these gases will resemble C_2F_6 or SF_6 and unit deactivation can be used for the high-pressure limit. Both of these factors can change the assignment of E_0 by ∼1 kcal mol^{-1}, since a 2 kcal mol^{-1} change in E_0 alters k_E(2,3-FH) by a factor of 2.3 and k_E(1,2-FH) by a factor of 2.6 for $\langle E_V \rangle \cong 97$ kcal mol^{-1}. The rate constants are not very sensitive to changes in structure of the transition states, and DFT calculations with different basis sets usually change k_E by less than 15% (for the same E_0), which would only change the threshold energy assignment by ∼0.5 kcal mol^{-1}. Andersson and Uvdal[18] have summarized the scaling factors for frequencies calculated from various basis sets. We have not employed any scaling factors, because their effects tend to cancel in the ratio of the sums and density of states. Application of scaling factors for frequencies calculated from 6-31G(d′,p′) for CF_3CFHCH_3, and transition states would only marginally change k_E. The calculation also is not very sensitive to the barrier employed for the internal rotation as shown by the comparisons in Figure 2 for hindered rotors vs free rotors. The deficiencies of eq 3 are those of transition-state theory and harmonic counts for density and sums of states. Such effects seem to be either minor or cancel based upon comparison of assigned threshold energies from eq 3 with those determined independently from thermal Arrhenius constants for several test-case fluoro- and chloro-ethane and -propane molecules.[4] Tunneling was not included in the above list, because extensive kinetic-isotope measurements[6] for $CF_3CFClCH_3$-d_0-d_1-d_2-d_3 suggest that tunneling is not important for 2,3-FH or 2,3-FD loss from highly vibrationally excited molecules. Extensive analysis of the primary and secondary (statistical) kinetic-isotope effects for HCl and HF elimination reactions can be found in refs 4 and 6.

The good agreement between the threshold energies assigned from independent measurements with CF_3CHFCH_3 and CF_3CHFCD_3 suggests that the overall uncertainty for E_0(2,3-FH) = 60.5 kcal mol^{-1} is ±1.5 kcal mol^{-1}. The larger experimental uncertainty in the data for the 1,2-FH reaction gives an uncertainty of ±2 kcal mol^{-1} for E_0(1,2-FH) = 73 kcal mol^{-1}. The ±2 kcal mol^{-1} uncertainty in $\langle E_V \rangle$ for CF_3CHFCH_3 is one of the more favorable cases for halopropanes formed by radical recombination. For some formation reactions,[19] the question of an energy barrier for radical recombination may augment the uncertainty of the thermochemistry.

4.2. Comparison of Threshold Energies for 2,3- and 1,2-FH Elimination Reactions. The 13−14 kcal mol^{-1} energy difference between E_0(1,2-FH) and E_0(2,3-FH) for CF_3CHFCH_3 resembles the difference between CF_3CH_3 (69 kcal mol^{-1}) and CFH_2CH_3 (58 kcal mol^{-1}). Substitution of a CF_3 group for a H atom in CFH_2CH_3 only raises the threshold energy for 2,3-FH elimination by 2−3 kcal mol^{-1}. The energy differences for both comparisons can be explained by the following two factors: First, the larger bond dissociation energy, *D*, for *D*(C−F) and *D*(C−H), which are 125 and 106 kcal mol^{-1}, respectively, for CF_3CH_3 compared to 108 and 98 kcal mol^{-1}, respectively, for CFH_2CH_3, is one cause for the higher $E_0(CF_3CH_3)$ relative to $E_0(CFH_2CH_3)$. The trend for the energies of the bonds that evolve to the four-membered transition states for 1,2-FH and 2,3-FH from CF_3CHFCH_3 would be similar. Second, the difference in bond energies of (sp^3)C−H versus (sp^2)C−H bonds for out-of-ring atoms is much larger than the corresponding difference for C−F bonds, especially for the CF_3 group as the sp^3(C−F) representative. The typical difference in energy for C−H bonds is about 13 kcal mol^{-1} in favor of the sp^2 bond, whereas the difference in energy between C−F bonds for CH_2-CF_2 or CH_2CHF and CF_3CH_3 is negligible. Thus, the transition state for CFH_2CH_3 with four (sp^2)C−H bonds will be stabilized more than the transition state for CF_3CH_3 with only two (sp^2)C−H bonds. The situation for 1,2-FH and 2,3-FH transition states is even more extreme with the 2,3-FH transition state having three (sp^2)C−H bonds and the 1,2-FH transition state having no (sp^2)C−H bonds. In addition the C−CF_3 bond will be stronger than the C−CH_3 bond, which further stabilizes the 2,3-FH transition state.

Computed structures, B3PW91 6-31G(d′,p′), for the transition state geometries for the two HF elimination channels of CF_3-$CHFCH_3$, Figure 2, support the arguments in the previous paragraph that were based on experimental bond dissociation energies and the assumption that the carbon atoms in the ring of the transition state had significant sp^2 character. Two sets of geometric parameters shown in Figure 2 are evidence for substantial sp^2 character in the 2,3-FH elimination transition state: (a) the angles between the C=C bond and the triangular plane defined by the H−C−H (157.3°) and the H−C−CF_3 (164.0°) are much closer to a sp^2 than sp^3 geometry and (b) the H−C−H and the H−C−CF_3 bond angles of the transitions state (117.7° and 113.3°, respectively) are very close to the corresponding angles in the $CF_3CH{=}CH_2$ product (117.5° and 114.3°, respectively). A similar conclusion emerges from analysis of the geometries of the 1,2-FH elimination transition state and the alkene product. In addition, the 16 kcal mol^{-1} lower energy computed for $CF_3CH{=}CH_2$ compared to $CF_2{=}CFCH_3$ is pleasingly close to the 13−14 kcal mol^{-1} difference in threshold energies and further illustrates the substantial sp^2 character of the carbons in the transition state. Finally, computed bond distances support the assertion that the C−H bond dissociation energies of the transition state are close to those for C−H bonds in alkenes. Figure 2 shows that computed bond distances for the out-of-ring C−H bonds in the 2,3-FH elimination transition state are the same as, or slightly shorter than, those in the alkene product.

The experimentally assigned threshold energies based upon chemical activation data for several reactions are summarized in Table 3 and compared to threshold energies from DFT calculations at the B3PW91/6-31G(d′,p′) level. The first thing to note is the close agreement between the experimental and calculated threshold energies for CF_3CHFCH_3 (and for several other reactions). This agreement is, in part, fortuitous because using larger basis sets generally lowers the calculated E_0 values and increases the discrepancy with experimental values,[4] whereas one would prefer the converse for the ideal computational model. The second general point is the ∼10 kcal mol^{-1} higher threshold energies for 1,2-FH relative to 2,3-FH reactions; the E_0(1,2-FH) values tend to be ≥70 kcal mol $^{-1}$. This 10 kcal mol^{-1} difference is a general feature of CF_3CXYCH_3 and the explanation is the same as given in detail above for CF_3CHFCH_3. A third general point is the 3−5 kcal mol $^{-1}$ increase of the threshold energy for 2,3-FH elimination upon replacement of the CH_3 group by the CF_3 group, e.g., compare CF_3CHFCH_3 to CH_3CHFCH_3 or $CH_3CF_2CH_3$. Adding one more F atom to the secondary carbon also increases E_0(2,3-FH) for $CF_3CF_2CH_3$ relative to CF_3CFHCH_3. This 5 kcal mol $^{-1}$ difference is a consequence of the difference of bond energies for CH_3 in the molecule and in the transition state versus those for a CF_3 group. The C−CF_3 bond energies are similar whereas the C−CH_3 bond energy increases in the transition states. The CF_3CHFCH_3 and CF_3CHFCF_3 molecules have slightly higher threshold energies for 1,2-FH elimination than CF_3CH_3 or CF_3CH_2F because of the difference in bond energies for the (sp^2)C−F versus the (sp^2)C−H.

The large rate constant and hence low E_0 for $CF_3CH_2CH_3$ seemed anomalous for 1,2-HF elimination.[4] The original data[1] for $CF_3CH_2CH_3$ were collected in 1998 using both $CF_3 + CH_2CH_3$ and $CF_3CH_2 + CH_3$ activation. These experiments have been recently repeated,[5] and the large rate constants could not be confirmed. Apparently the pressure measurements of the work in 1998 were in error by an order of magnitude due to using an incorrect range on the MKS electronic manometer, and the new rate constants are about 10 times smaller for both energies. Thus, $E_0 = 64$ kcal mol^{-1} assigned[4] by fitting the rate constants from 1998 must be revised. On the basis of the new data, the E_0(1,2-FH) for $CF_3CH_2CH_3$ will be 68−69 kcal mol^{-1}. With these new experimental results, the discrepancy between the calculated and experimentally derived values for the threshold energy disappears. The addition of the fourth F atom to $CF_3CH_2CH_3$ clearly raises E_0 for 1,2-FH elimination from CF_3CHFCH_3, as noted above. The $CF_3CH_2CF_3$−CF_3CHFCF_3 pair can be compared for the effect upon E_0 of adding a seventh F atom for 1,2-FH elimination. The calculations suggest that E_0 should increase by ~5 kcal mol^{-1}; the experimental results suggest a more modest increase for CF_3CHFCF_3 relative to $CF_3CH_2CF_3$. Although the experimental data are limited,[5] it seems safe to conclude that CF_3CHFCF_3 has the highest threshold energy of any fluoropropane. This trend of increasing E_0 values with greater F-atom content is consistent with that for fluoroethanes.

Finding and resolving the discrepancy in E_0 for $CF_3CH_2CH_3$ illustrates the importance of having both experimental and calculated threshold energies for a series of molecules. The B3PW91/6-31G(d′,p′) calculated E_0's are usually close to the experimental result; however, the calculated E_0(1,2-FH) for $CF_3CH_2CH_2Cl$, $CF_3CH_2CF_3$ and CF_3CHFCH_3 are all 3−4 kcal mol^{-1} lower than the experimental values. We must conclude that the calculated threshold energies at the DFT B3PW91/6-31G(d′,p′) level, although showing the correct trends in E_0 values, are not always quantitatively reliable. This is not surprising because there is no lower bound to the transition state energy and hence using larger basis sets does not necessarily improve the computed E_0 values.

5. Conclusions

The unimolecular 1,2-FH and 2,3-FH elimination reactions of CF_3CHFCH_3 have been characterized using the chemical activation technique for an average vibrational energy of 97 kcal mol^{-1}. The transition states were modeled by DFT calculations at the B3PW91/6-31G(d′,p′) level. The transition state for 1,2-FH elimination has a 2-fold larger pre-exponential factor than for 2,3-HF elimination, because three F atoms attached to carbon atoms of the four-membered ring have lower frequencies than those in a CF_3 group. The experimental kinetic-isotope effect for 2,3-FD elimination from CF_3CHFCD_3 is 2.8 and the transition-state models reproduce this isotope effect. The computed transition state structures show a nearly planar four-membered ring and substantial planarity of the four out-of-ring atoms attached to the C=C bond, indicative of significant sp^2 character for the carbons. Results from the DFT calculations were used with the RRKM theory, employing a hindered internal rotor treatment of the torsional motions, to compute rate constants that fitted the experimental results using threshold energies of 60.5 ± 1.5 and 73 ± 2 kcal mol^{-1} for 2,3-FH and 1,2-FH elimination, respectively. The 13−14 kcal mol^{-1} lower threshold energy for 2,3-FH versus 1,2-FH elimination is mainly a consequence of the difference in bond energies of (sp^3)C−X versus (sp^2)C−X bonds for the four out-of-ring atoms (X = C, H, or F). For X = H the bonds are stronger for sp^2 versus sp^3 carbons but for X = F or C the corresponding bond energies are similar. These principles also can be used when comparing threshold energies for different molecules. For example, the 1,2-FH elimination reaction of $CF_3CH_2CH_3$, which has been reinvestigated,[5] can be compared to CF_3CHFCH_3. The replacement of H by an F atom in the secondary position raised the threshold energy for 1,2-FH elimination by ~3 kcal mol^{-1}. The threshold energy for 1,2-FH elimination from CF_3CFHCH_3 is ~4 kcal mol^{-1} higher than for CF_3CH_3 or CF_3CH_2F. Comparison of the 2,3-FH elimination threshold energy for CF_3CHFCH_3 with CH_2FCH_3 and CH_3CHFCH_3 shows that substituting a CF_3 group for a H or a CH_3, respectively, raises the threshold energy by 2−3 kcal mol for CH_3CH_2F and 4−5 kcal mol^{-1} for CH_3CHFCH_3.

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References and Notes

(1) Ferguson, H. A.; Ferguson, J. D.; Holmes, B. E. *J. Phys. Chem. A* **1998**, *102*, 5393.

(2) McDoniel, J.; Bridget; Holmes, B. E. *J. Phys. Chem. A* **1997**, *101*, 1334.

(3) (a) Burgin, M. O.; Heard, G. L.; Martell, J. M.; Holmes, B. E. *J. Phys. Chem. A* **2001**, *105*, 1615. (b) Heard, G. L.; Holmes, B. E. *J. Phys. Chem. A* **2001**, *105*, 1622.

(4) Ferguson, J. D.; Johnson, N. L.; Kekenes-Huskey, P. M.; Everett, W. C.; Heard; G. L.; Setser, D. W.; Holmes, B. E. *J. Phys. Chem. A* **2005**, *109*, 4540.

(5) Roach, M. S.; Sibila, B. M.; Holmes, B. E. *J. Phys. Chem. A* **2005**, submitted.

(6) Zhu, Li; Simmons, J. G., Jr.; Burgin, M. O.; Setser, D. W.; Holmes, B. E.; *J. Phys. Chem. A* **2005**, in press.

(7) Martell, J. M.; Beaton, P. J.; Holmes, B. E. *J. Phys. Chem. A* **2002**, *106*, 8471.

(8) (a) Beaver, M. R.; Heard, G. L.; Holmes, B. E. *Tetrahedron Lett.* **2002**, *43*, 8075. (b) Burgin, M. O.; Simmons, J. G., Jr.; Heard, G. L.; Setser, D. W.; Holmes, B. E. *J. Phys. Chem. A* **2005**, to be submitted.

(9) Rajakumar, B.; Arunan, E. *Phys. Chem. Chem. Phys.* **2003**, *5*, 8892.

(10) Zachariah, M. R.; Westmoreland, P. R.; Burgess, D. R., Jr.; Tsang, W.; Melius, C. F. *J. Phys. Chem.* **1996**, *100*, 8737.

(11) Zhang, X.-M. *J. Org. Chem.* **1998**, *63*, 3590.

(12) Chandra, A. K.; Uchimaru, T. *J. Phys. Chem. A* **2000**, *104*, 9244.

(13) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(14) (a) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience, New York, 1st ed. 1972, 2nd ed. 1996. (b) Baer, T.; Hase, W. L. *Unimolecular Reaction Dynamics: Theory and Experiments*; Oxford University Press: New York, 1996.

(15) Barker, J. R. *Int. J. Chem. Kinet.* **2001**, *33*, 232.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kuden, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Bega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratman, R. E.; Yazyev, O.; Austen, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewksi, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malik, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(17) Yamada, T.; Lay, T. H.; Bozzelli, J. W. *J. Phys. Chem. A* **1998**, *102*, 7286.

(18) Andersson, M. P.; Uvdal, P. *J. Phys. Chem. A* **2005**, *109*, 2937.

(19) Dils, B.; Vertommen, J.; Carl, S. A.; Vereecken, L.; Peaters, I. *J. Phys. Chem. Chem. Phys.* **2005**, *7*, 1187.

(20) Millward, G. E.; Tschuikow-Roux, E. *J. Phys. Chem.* **1997**, *76*, 2292.