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Unimolecular Reactions Including ClF Interchange of Vibrationally Excited $CF_2ClCHFCH_2CH_3$ and $CF_2ClCHFCD_2CD_3$

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Vibrationally excited $CF_2ClCHFC_2H_5$($CF_2ClCHFC_2D_5$) molecules were prepared in the gas phase at 300 K with ≈93 kcal mol^{-1} of energy by recombination of CF_2ClCHF and C_2H_5 or C_2D_5 radicals. Three unimolecular reactions were observed. 1,2-ClF interchange converts $CF_2ClCHFC_2H_5$($CF_2ClCHFC_2D_5$) into $CF_3CHClC_2H_5$($CF_3CHClC_2D_5$), and subsequent 2,3-ClH (ClD) elimination gives $CF_3CH{=}CHCH_3$ ($CF_3CH{=}CDCD_3$). 2,3-FH(FD) elimination gives *cis*- and *trans*-$CF_2ClCH{=}CHCH_3$ ($CF_2ClCH{=}CDCD_3$), and 1,2-ClH elimination gives $CF_2{=}CFCH_2CH_3$ ($CF_2{=}CFCD_2CD_3$). The experimental rate constants for $CF_2ClCHFC_2H_5$ ($CF_2ClCHFC_2D_5$) were 1.3×10^4 (0.63×10^4) s^{-1} for 1,2-FCl interchange and 2.1×10^4 (0.61×10^4) s^{-1} with a *trans/cis* ratio of 3.7 for 2,3-FH(FD) elimination. The 1,2-ClH process was the least important with a branching fraction of only 0.08 ± 0.04. The rate constants for 2,3-ClH (ClD) elimination from $CF_3CHClC_2H_5$ ($CF_3CHClC_2D_5$) were 1.8×10^6 (0.49×10^6) s^{-1} with a *trans*/*cis* ratio of 2.4. Density functional theory was used to compute vibrational frequencies and structures needed to obtain rate constants from RRKM theory. Matching theoretical and experimental rate constants provides estimates of the threshold energies, E_0, for the three reaction pathways; 1,2-FCl interchange has the lowest E_0. The unimolecular reactions of $CF_2ClCHFC_2H_5$ are compared to those of $CF_2ClCHFCH_3$. Both of these systems are compared to $CH_3CHFC_2H_5$ to illustrate the influence of a CF_2Cl group on the E_0 for FH elimination.

1. Introduction

The unimolecular interchange reaction of F and Cl atoms located on adjacent carbon atoms has been demonstrated for $CF_2ClCF_2CH_3(CD_3)$ and $CF_2ClCHFCH_3(CD_3)$.[1−3] The 1,2-ClF interchange process is competitive with HCl and HF elimination reactions for vibrational energies of ≈95 kcal mol^{-1}. In the present work we have extended the investigation of ClF interchange reactions to $CF_2ClCHFC_2H_5$ and $CF_2ClCHFC_2D_5$ formed by recombination of CF_2ClCHF and $C_2H_5(C_2D_5)$ radicals. In addition to providing a third definitive example of ClF interchange, the data provide an opportunity to study the difference between a CH_3 group and a C_2H_5 group on the E_0 of the Cl−F interchange transition state, which has a bridged structure with the Cl and F atoms located above and below the plane of the carbon atoms with a nearly sp^2 type structure.[1,2]

In recent publications experimental unimolecular rate constants measured at a fixed vibrational energy for several fluorochloroethanes and -propanes have been matched to calculated RRKM rate constants to assign E_0.[1,4−7] In this application of RRKM theory, vibrational frequencies and rotational moments of inertia were obtained from density functional theory (DFT) calculations of electronic structures; torsional motions were treated as hindered internal rotations in the evaluation of sums and densities of states.[4] We have argued that the E_0 assignments from reliable chemical activation data[6] have uncertainties of ±1.5 kcal mol^{-1}. Application of this methodology to $CF_2ClCHFC_2H_5$ is considerably more labor intensive because several conformers exist for both the molecule and transition states. The data also are less reliable than for the propanes, because the rate constants are smaller, thus requiring experiments at lower pressure. The state counting for RRKM calculations was done for structures corresponding to an average conformer of the molecule and the lowest energy conformer for transition states, and the assignment of threshold energies is less rigorous than for the ethane and propane systems previously studied.[1,4−7] A principal experimental objective was to identify and measure the rearranged product molecule $CF_3CHClC_2H_5$ ($CF_3CHClC_2D_5$) as proof of the 1,2-ClF interchange reaction. In anticipation of the data to be presented, the 1,2-FCl interchange reaction is a major unimolecular reaction for $CF_2ClCHFC_2H_5(C_2D_5)$. Although the evidence is indirect, Cl−F interchange reactions also occur in fluorochloroethanes.[8−10] The rate constants and threshold energies for the unimolecular reactions of $CF_2ClCHFC_2H_5$ are compared to those of $CF_2ClCHFCH_3$[1] and $CH_3CHFC_2H_5$.[11] and the nature of the ClF interchange and FH elimination transition states is discussed.

The chemically activated $CF_2ClCHFC_2H_5$ ($CF_2ClCHFC_2D_5$) molecules were prepared by the recombination of CF_2ClCHF and CH_2CH_3 (CD_2CD_3) radicals; reaction (1) at room temperature. The radicals were produced by photolysis of $CF_2ClCHFI$ and $C_2H_5I(C_2D_5I)$. The expected products from disproportionation and self-combination reactions were observed, but those reactions will not be listed.

$$CF_2ClCHF\bullet + CH_3CH_2\bullet \text{ (or } CD_3CD_2\bullet) \rightarrow CF_2ClCHFC_2H_5^* \text{ (or } CF_2ClCHFC_2D_5^*) \quad (1)$$

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No products were observed that would be expected from CF_3CHCl radicals, and the CF_2ClCHF radical does not isomerize under our experimental conditions. The asterisk denotes vibrationally excited molecules with 93 kcal mol^{-1} of internal energy. The unimolecular reaction pathways and collisional stabilization for $CF_2ClCHFC_2H_5$* are shown in reactions 2−6. A similar set of reactions exist for $CF_2ClCHFC_2D_5$*.

$$CF_2ClCHFC_2H_5^* \xrightarrow{k_{2,3-FH}} cis\text{- and } trans\text{-}CF_2ClCH{=}CHCH_3 + HF \quad (2)$$

$$\xrightarrow{k_{1,2-ClF}} CF_3CHClC_2H_5^* \quad (3)$$

$$\xrightarrow{k_{1,2-ClH}} CF_2{=}CFC_2H_5 + HCl \quad (4)$$

$$\xrightarrow{k_{1,2-FH}} cis\text{- and } trans\text{-}CFCl{=}CFC_2H_5 + HF \quad (5)$$

$$\xrightarrow{k_m[M]} CF_2ClCHFC_2H_5 \quad (6)$$

Since the enthalpy of reaction 3 is about −11 kcal mol^{-1}, $CF_3CHClC_2H_5$* contains ≈104 kcal mol^{-1} and reactions 7−9 can be anticipated.[2]

$$CF_3CHClC_2H_5^* \xrightarrow{k_{2,3-ClH}} cis\text{- and } trans\text{-}CF_3CH{=}CHCH_3 + HCl \quad (7)$$

$$\xrightarrow{k_{2,1-FCl}} CF_2ClCHFC_2H_5 \quad (8)$$

$$\xrightarrow{k_m[M]} CF_3CHClC_2H_5 \quad (9)$$

The threshold energy for 1,2-FH elimination is higher than those of competing processes, and reaction 5 and the corresponding step for $CF_3CHClC_2H_5$ were not observed. Since the reverse step, reaction 8, is slower than 2,3-ClH elimination, collisional stabilization and HCl elimination are the only options for $CF_3CHClC_2H_5$*. Experimental rate constants were obtained in the usual way from linear plots of the ratios of the decomposition product (D_i) to the stabilized product (S) vs pressure^{-1}.

2. Experimental Methods

$CF_2ClCHFC_2H_5$ ($CF_2ClCHFC_2D_5$) molecules were prepared by photolysis of mixtures typically containing 0.022 μmol of $CF_2ClCHFI$, 0.36 μmol of CH_3CH_2I or CD_3CD_2I, plus small amounts of mercury(I) iodide. The photolysis experiments were done at room temperature in Pyrex vessels ranging in volume from 530 to 4900 cm^3. To achieve higher pressures, 0.058 μmol of $CF_2ClCHFl$ and 0.51 μmol of CH_3CH_2I or CD_3CD_2I were used in these vessels. Samples were prepared by evacuating the photolysis vessel and then transferring premeasured gases to the vessel with cryogenic pumping. All gases were transferred on grease-free vacuum lines and a MKS type 270C high accuracy signal conditioner was used to measure pressures. Either a high-pressure Oriel 6137 arc lamp operated with a 200 W mercury lamp or an Oriel 58811 arc lamp operated with a 200 W HgXe lamp was used to photolyze mixtures for 2.2 to 8.7 min, depending on vessel volume, yielding approximately 10% conversion of reactants to products.

Products were identified with a Shimadzu QP5000 GC/MS equipped with a 120 m Rtx-VMS column (two 60 m columns in series). The following products were identified: $CF_2{=}CFCH_2CH_3$ (from 1,2-ClH elimination), *cis*- and *trans*-$CF_2ClCH{=}CHCH_3$ (from 2,3-FH elimination), *cis*- and *trans*-$CF_3CH{=}CHCH_3$ (from 1,2-FCl interchange, followed by 2,3-ClH elimination), $CF_2ClCHFC_2H_5$, and $CF_3CHClC_2H_5$ (from 1,2-FCl interchange followed by collisional stabilization). Commercial samples of *cis*- and *trans*-$CF_3CH{=}CHCH_3$ were used to identify this pair of products. A sample of *cis*- and *trans*-$CF_2ClCH{=}CHCH_3$ was prepared to verify those products. The synthesis involved the addition of CF_2Cl radicals, obtained from photolysis of 1,3-dichlorotetrafluoroacetone, to propene to obtain the $CF_2ClCH_2CHCH_3$ radical. Then a disporportionation reaction between CF_2Cl and $CF_2ClCH_2CHCH_3$ radicals produced *cis*- and *trans*-$CF_2ClCH{=}CHCH_3$ and CHF_2Cl. All other products were verified by mass spectral fragmentation patterns, which are shown in Table 1. Although authentic samples of $CF_2ClCHFC_2H_5$ and $CF_3CHClC_2H_5$ were unavailable, the GC retention times and mass spectral fragmentation patterns were consistent with expectations. For example, a prominent ion in the mass spectrum of $CF_2ClCHFC_2H_5$ is $C_3FH_5^+$ (m/e = 61), formed by breaking the C−C bond between the first and second carbons. The corresponding fragmentation in $CF_3CHClC_2H_5$, $C_3ClH_6^+$ (m/e = 77 and 79 for Cl-35 and Cl-37), was present with a relative abundance of 17 and 6, respectively. The deuterated molecule fragmented similarly with m/e values increased by 5. Identification of $CF_3CHClC_2H_5$ was also supported by the dependence of its yield on pressure; $CF_3CHClC_2H_5$ was not observed at high pressures because of collisional stabilization of $CF_2ClCHFC_2H_5$*, it was present in small concentrations at intermediate pressures, and it disappeared at low pressures because of decomposition.

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

m/e	RA	assignment	m/e	RA	assignment
	$CF_2{=}CFCH_2CH_3$			*cis*-$CF_2ClCH{=}CHCH_3$	
95	100	$C_3F_3H_2^+$	91	100	$C_4F_2H_5^+$
69	61	CF_3^+	39	44	$C_3H_3^+$
110	32	$C_4F_3H_5^+$	51	30	CF_2H^+
39	27	$C_3H_3^+$	71	29	$C_4FH_4^+$
27	24	$C_2H_3^+$	41	19	$C_3H_5^+$
	$CF_2{=}CFCD_2CD_3$			*cis*-$CF_2ClCH{=}CDCD_3$	
97	100	$C_3F_3D_2^+$	95	100	$C_4F_2D_4H^+$
69	70	CF_3^+	32	22	$C_2D_4^+$
115	31	$C_4F_3D_5^+$	74	16	$C_4FD_3H^+$
30	27	$C_2D_3^+$	30	14	$C_2D_3^+$
50	24	CF_2^+	45	12	$C_3D_4H^+$
	trans-$CF_2ClCH{=}CHCH_3$			$CF_2ClCHFCH_2CH_3$	
91	100	$C_4F_2H_5^+$	61	100	$C_3FH_6^+$
39	41	$C_3H_3^+$	29	42	$C_2H_5^+$
51	35	CF_2H^+	27	35	$C_2H_3^+$
71	28	$C_4FH_4^+$	47	31	$C_2FH_4^+$
41	19	$C_3H_5^+$	41	28	$C_3H_5^+$
	trans-$CF_2ClCH{=}CDCD_3$			$CF_2ClCHFCD_2CD_3$	
95	100	$C_4F_2D_4H^+$	66	100	$C_3FD_5H^+$
74	21	$C_4FD_3H^+$	34	39	$C_2D_5^+$
41	20	$C_3D_2H^+$	30	23	$C_2D_3^+$
45	19	$C_3D_4H^+$	51	23	CF_2H^+
30	17	$C_2D_3^+$	45	21	$C_3D_4H^+$
	$CF_3CHClCH_2CH_3$			$CF_3CHClCD_2CD_3$	
29	100	$C_2H_5^+$	34	100	$C_2D_5^+$
41	27	$C_3H_5^+$	82	25	$C_3{}^{35}ClHD_5^+$
110	21	$C_4F_4H_5^+$	45	22	$C_3D_4H^+$
77	17	$C_3{}^{35}ClH_6^+$	30	19	$C_2D_3^+$
32	13	CFH^+	114	17	$C_4F_3D_4H^+$

Both a Shimadzu GC-14A gas chromatograph with flame ionization detection operated with a 105 m Rtx-VGC column of 0.53 mm inner diameter and a Shimadzu QP5000 gas chromatograph with mass spectrometric detector, operated with a 120 m Rtx-VMS column, were used to measure the ratios of decomposition to stabilization products (D_i/S) at various pressures. Similar temperature programs were used in each GC; the oven was at 35 °C for 20 min, and then the temperature was increased to 170 °C at a rate of 8 °C/min. Retention times for compounds of interest are as follows: C_4H_{10} at 12.0 min; $CF_2{=}CFC_2H_5$ at 17.0 min; *cis*-$CF_3CH{=}CHCH_3$ at 17.3 min; *trans*-$CF_3CH{=}CHCH_3$ at 17.7 min; *cis*-$CF_2ClCH{=}CHCH_3$ at 30.2 min; $CF_3CHClCH_2CH_3$ at 30.7 min; *trans*-$CF_2ClCH{=}CHCH_3$ at 31.5 min; $CF_2ClCHFC_2H_5$ at 35.7 min; CH_3CH_2I at 36.8 min; $CF_2ClCHFI$ at 42.8 min; *meso*- and *d,1*-$CF_2ClCHFCHFCF_2Cl$ at 39.1 and 42.2 min. The *meso* and *d,1* pair are indistinguishable, thus the order of elution of these two products is uncertain. The GC-FID procedure completely resolved only *trans*-$CF_3CH{=}CHCH_3$, *trans*-$CF_2ClCH{=}CHCH_3$, $CF_2ClCHFC_2H_5$, and $CF_3CHClC_2H_5$. Therefore, the GC/MS was utilized to collect data for the *cis*-olefins and for $CF_2{=}CFC_2H_5$ by comparison to the *trans*-olefins. Because some compounds were not completely resolved, the total ion current could not be integrated (in some cases) and parent and daughter ions had to be monitored.

The primary data for measuring the D_i/S ratios were obtained with the GC/FID system. The ratio of response factors for halogenated alkene and alkanes that differ only by loss of HCl or HF are nearly unity for flame ionization detection.[4] We confirmed this response factor by comparing six samples of mixtures of $CF_3CF{=}CH_2$ and $CF_3CF_2CH_3$ and three samples of mixtures of $CF_3CH{=}CH_2$ and $CF_3CH_2CH_2Cl$. The two pairs were chosen because the fluoroalkene is formed from the fluoroalkane by the loss of HF or HCl; the ratios of response factors were 0.95 (±0.02) and 1.00 (±0.01), respectively. These tests indicated nearly equal response for halopropene versus halopropanes to flame ionization detection, and we adopted a ratio of unity as the response factor for halobutenes and halobutanes, which should introduce less than 10% uncertainty in a given D_i/S ratio.

Since GC-FID data could be used only to assign *trans*-$CF_3CH{=}CHCH_3/CF_3CHClC_2H_5$, *trans*-$CF_2ClCH{=}CHCH_3/CF_2ClCHFC_2H_5$, and $CF_3CHClC_2H_5/CF_2ClCHFC_2H_5$ ratios, the response factors for halogenated alkenes from mass spectral detection must be considered to complete the analysis. Equivalent responses for *cis*-$CF_2ClCH{=}CHCH_3$ and *trans*-$CF_2ClCH{=}CHCH_3$ (or *cis*-$CF_2ClCH{=}CDCD_3$ and *trans*-$CF_2ClCH{=}CDCD_3$) were confirmed from authentic samples. Similarly, *cis*-$CF_3CH{=}CHCH_3$ and *trans*-$CF_3CH{=}CHCH_3$ (or *cis*-$CF_3CH{=}CDCD_3$ and *trans*-$CF_3CH{=}CDCD_3$) had equal responses.

The $CF_2{=}CFC_2H_5$ yield was assigned by comparing the total ion currents of $CF_2{=}CFC_2H_5$ and *trans*-$CFClCH{=}CHCH_3$. This comparison assumes that the ionization cross sections for the two olefins are equal. Because the yield of $CF_2{=}CFC_2H_5$ was low, the uncertainty in its measurement is greater than for other products.

3. Computational Methods

Density function theory (DFT) calculations were performed using the GAUSSIAN 03[12] suite of programs. All ground-state and transition-state geometries were optimized, along with calculations of vibrational frequencies, zero-point vibrational energies, and overall rotational moments of inertia. Calculations were performed using the B3PW91 method with the 6-31G(d′,p′) basis set. Description of these methods as used in our laboratory can be found in refs 2 and 13. The structures and vibrational frequencies obtained from different basis sets for molecules and transition states have been found to be in close agreement, and we employed results from the (d′,p′) basis set for rate constant calculations to be consistent with previous work.[1,4−6] Other basis sets also were used in isodesmic calculations to estimate the $\Delta H^\circ_f(CF_2ClCHFC_2H_5)$ and the enthalpy of reaction (3).

The $CF_2ClCHFC_2H_5$, $CF_3CHClC_2H_5$, and $CH_3CHFC_2H_5$ molecules and their transition states have several conformers. The energies of the three conformers for $CH_3CHFC_2H_5$ were explored with both DFT and MP2 calculations. The differences in energy among the three conformers for the two methods were less than 0.5 kcal mol^{-1}. Our calculated results for $CH_3CHFC_2H_5$ also agreed with experimental measurements and calculations of ref 14. Therefore, we calculated frequencies and moments of inertia for all conformers, which were then averaged to calculate the density of states of a representative conformer for $CH_3CHFC_2H_5$, $CF_3CHClC_2H_5$, and $CF_2ClCHFC_2H_5$. The torsional motions of the CF_2Cl (or CF_3) and C_2H_5 groups were treated as symmetric hindered internal rotations; the torsional motion of the CH_3 group was treated as a vibration. The reduced moments for internal rotation were calculated for the geometry of the conformers and then averaged. The barriers to internal rotation of the molecules were obtained by identification of the maximum positions of the potentials for internal rotation. These calculations were done at the B3PW91/6-31G(d′,p′) level. The barriers calculated for the $-C_2H_5$ group in $CH_3CHFC_2H_5$ were in agreement with those calculated in ref 14. Calculated structures of the conformers are in Table S1 (Supporting Information), and vibrational frequencies for each conformer and for the average representative conformer are provided in Table S2 (Supporting Information).

The conformers of the transition states associated with C_2H_5 internal rotation (for 1,2-ClF or 1,2-ClH processes) or with CF_2Cl internal rotation (for 2,3-FH elimination) were difficult to define for some configurations. Since the vibrational frequencies of different conformers are very similar, we decided to use the results of just the lowest energy conformer for the transition states. The computed results including the reduced moments of internal rotation and the potential barriers are given in Table S4 of the Supporting Information. The molecular and transition state dipole moments and Mulliken charges of the individual atoms in each molecule and the lowest energy conformer for each transition state were calculated using the B3LYP density at the optimized geometry, and these are also given in Table S1.

Vibrational frequencies and moments of inertia from the DFT calculations were used with RRKM theory to calculate rate constants, k_E, and kinetic-isotope effects, k_{EH}/k_{ED}.

$$k_E = \left(s^{\ddagger}/h\right)\left(I^{\ddagger}/I\right)^{1/2}\left(\sum P^{\ddagger}(E - E_0)/N_E^*\right) \qquad (10)$$

The sums of states for the transition state, $\sum P^{\ddagger}(E - E_0)$, and the density of states for the molecule, N_E^*, were calculated with the Multiwell code.[15] The reaction path degeneracy is $s^{\ddagger}$, and $I^{\ddagger}/I$ is the ratio of the three overall rotational moments of inertia. The only unknown factor in eq 11 is the threshold energy, which is determined by matching $k_{\langle E\rangle}$ and k_{expt}. The pre-exponential factors, in partition function form with $s^{\ddagger} = 1.0$, of the thermal rate constants also were examined for the three reaction paths of $CF_2ClCHFC_2H_5$ to ensure conformity with the models for $CF_2ClCHFCH_3$;[1] the values at 1000 K are 0.69×10^{13} s^{-1}, 2.2×10^{13} s^{-1}, and 0.83×10^{13} s^{-1} for 1,2-ClF interchange, 1,2-ClH elimination, and 2,3-FH elimination, respectively.

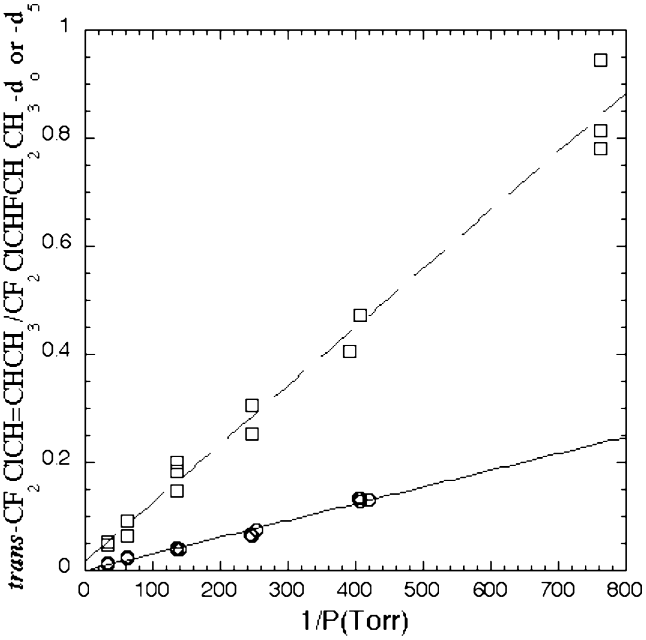

Figure 1. Plots of *trans*-$CF_2ClCH{=}CHCH_3/CF_2ClCHFC_2H_5$ (□) and *trans*-$CF_2ClCH{=}CDCD_3/CF_2ClCHFC_2D_5$ (○) vs pressure^{-1}. The slopes (intercepts) are $(1.08 \pm 0.04) \times 10^{-3}$ Torr (0.018 ± 0.013) and $(0.309 \pm 0.011) \times 10^{-3}$ Torr (0.0006 ± 0.0026) for $CF_2ClCHFC_2H_5$ and $CF_2ClCHFC_2D_5$, respectively. The correlation coefficient is 0.992 for both plots.

4. Results

4.1. Experimental Rate Constants. The *cis/trans* ratios of product olefins can vary with pressure for chemically activated haloalkane systems that involve carbene intermediates in the decomposition mechanism. For example, 1,1-HX elimination from $CHCl_2CH_2Cl$[16] and CHF_2CH_2F[17] produced *cis/trans* ratios that varied by factors of 2.5 and 2.0 with pressure, respectively. No variations in the *cis/trans* ratios were observed from the $CF_2ClCHFC_2H_5(C_2D_5)$ systems, and the reaction mechanism already presented seems adequate.

The primary data are the GC/FID measurements of ratios of *trans*-$CF_2ClCH{=}CHCH_3/CF_2ClCHFC_2H_5$, *trans*-$CF_3CH{=}CHCH_3/CF_2ClCHFC_2H_5$, and *trans*-$CF_3CH{=}CHCH_3/CF_3CHClC_2H_5$ vs inverse pressure; see Figures 1 and 2. Due to concern about the vapor pressure of Hg_2I_2 and the $Hg + Hg_2I_2$ mixture, no experiments were attempted for pressures below 1×10^{-3} Torr. Plots of the *trans*-$CF_2ClCH{=}CDCD_3$ and *trans*-$CF_3CH{=}CDCD_3$ data also are shown in Figures 1 and 2 from $CF_2ClCHFC_2D_5$ and $CF_3CHClC_2D_5$. The rate constants for *trans*-2,3-FH and *trans*-2,3-FD elimination are 1.08 and 0.31×10^{-3} Torr, respectively. To obtain the total 2,3-FH(FD) rate constants, the *trans/cis* ratio from the mass spectral data is required. Figure 3 shows the *trans/cis* ratios for $CF_2ClCH{=}CHCH_3$ and $CF_2ClC{=}CHCD_3$; the ratios are independent of pressure with *trans*-$CF_2ClCH{=}CHCH_3$/*cis*-$CF_2ClCH{=}CHCH_3$ = 3.7 and *trans*-$CF_2ClCH{=}CDCD_3$/*cis*-$CF_3CH{=}CDCD_3$ = 3.8. Scaling the rate constant for *trans*-2,3-FH(FD) elimination by a factor of 1.3 to account for the *cis* product gives a total rate constant for 2,3-FH(FD) elimination of 1.4×10^{-3} (0.40×10^{-3}) Torr, as shown in Table 2. The data for $CF_2ClCHFC_2D_5$ only extend to $D_i/S < 0.14$, and the uncertainty in k(2,3-FD) could be rather large.

The data for $CF_3CHClC_2H_5$ (C_2D_5) in Figure 2 correspond to a high extent of decomposition. If cascade collisional deactivation occurs, such data may overestimate the unit deactivation rate constant.[18,19] The apparent rate constants for *trans*-$CF_3CH{=}CHCH_3$ and *trans*-$CF_3CH{=}CHCD_3$ are 0.082 and 0.023 Torr, respectively, and scaling for *cis*-$CF_3CH{=}CHCH_3(CD_3)$ gives total rate constants for 2,3-ClH(ClD) elimination of 0.12 (0.035) Torr. For the $CF_2ClCHFC_2H_5$ series of experiments, the *cis*-$CF_3CH{=}CHCH_3$ product peak actually was resolved by the GC/FID, and these results also are shown in Figure 2. The ratio of *trans*-$CF_3CH{=}CHCH_3$ to *cis*-$CF_3CH{=}CHCH_3$ from the data of Figure 2 is 2.34, which agrees with the mass spectrometrically measured ratio in Figure 3.

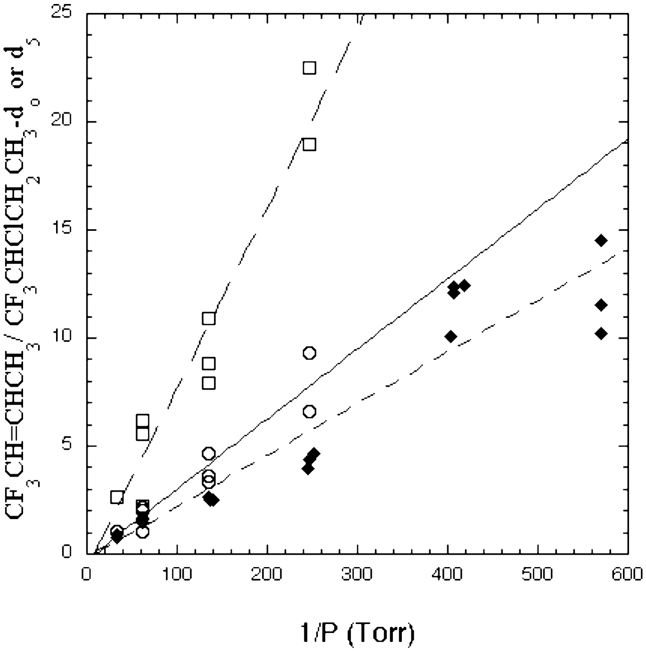

Figure 2. Plots of *trans*- (□) and *cis*-$CF_3CH{=}CHCH_3/CF_3CHClC_2H_5$ (○) and *trans*-$CF_3CH{=}CDCD_3/CF_3CHClC_2D_5$ (◆) vs pressure^{-1}. The *cis*-$CF_3CH{=}CHC_2D_5$ yield was too low to be accurately measured by FID/GC in this series of experiments. The slope (intercept) for the $CF_3CHClC_2H_5$ plot are 0.082 ± 0.007 Torr (-0.65 ± 0.92) for *trans* and 0.034 ± 0.007 Torr (-0.20 ± 0.42) for *cis*. The slopes and intercepts for $CF_3CHClC_2D_5$ are 0.023 ± 0.002 Torr and -0.18 ± 0.62 for the *trans*-$CF_3CH{=}CDCD_3$ plot. The large *D/S* ratios are a consequence of the small degree of collisional stabilization of $CF_3CHClC_2H_5$* or $CF_3CHClC_2D_5$*. The correlation coefficients were between 0.95 and 0.97 for the plots.

The 1,2-ClF interchange rate constants were obtained by scaling the *trans*-$CF_3CH{=}CHCH_3$ yield by 1.4 to account for *cis*-$CF_3CH{=}CHCH_3$ and adding the measured small contribution of $CF_3CHClC_2H_5$ to obtain the total D_i. The stabilized product was directly measured by GC/FID, and the resulting D_i/S plots shown in Figure 4 give rate constants of 0.85×10^{-3} (0.42×10^{-3}) Torr for $CF_2ClCHFC_2H_5(C_2D_5)$. The 2,3-FD and 1,2-ClF rate constants are equal for $CF_2ClCHFC_2D_5$, and Cl−F interchange clearly is an important reaction channel.

The rate constant for 1,2-ClH elimination was estimated from the average ratio of $CF_2{=}CFC_2H_5$ to *trans*-$CF_2ClCH{=}CHCH_3$. The ratio of the most abundant ions from each product from the mass spectrometric data was scaled by 1.3 to obtain the ratio of total ion currents from these two product olefins, which is assumed to be equal to the ratio of their concentrations. The ratio of $CF_2{=}CHC_2H_5$ to *trans*-$CF_2ClCH{=}CHCH_3$ from Figure 3A is 0.18 ± 0.06, which corresponds to a rate constant of $(0.20 \pm 0.06) \times 10^{-3}$ Torr or $(0.29 \pm 0.10) \times 10^{4}$ s^{-1} for 1,2-ClH elimination from $CF_2ClCHFC_2H_5$. This rate constant corresponds to a branching fraction of 0.08 ± 0.04, and 1,2-ClH elimination is a minor reaction channel. Although $CF_2{=}CHC_2D_5$ was observed, the yield was too low to be measured reliably, and no rate constant can be reported.

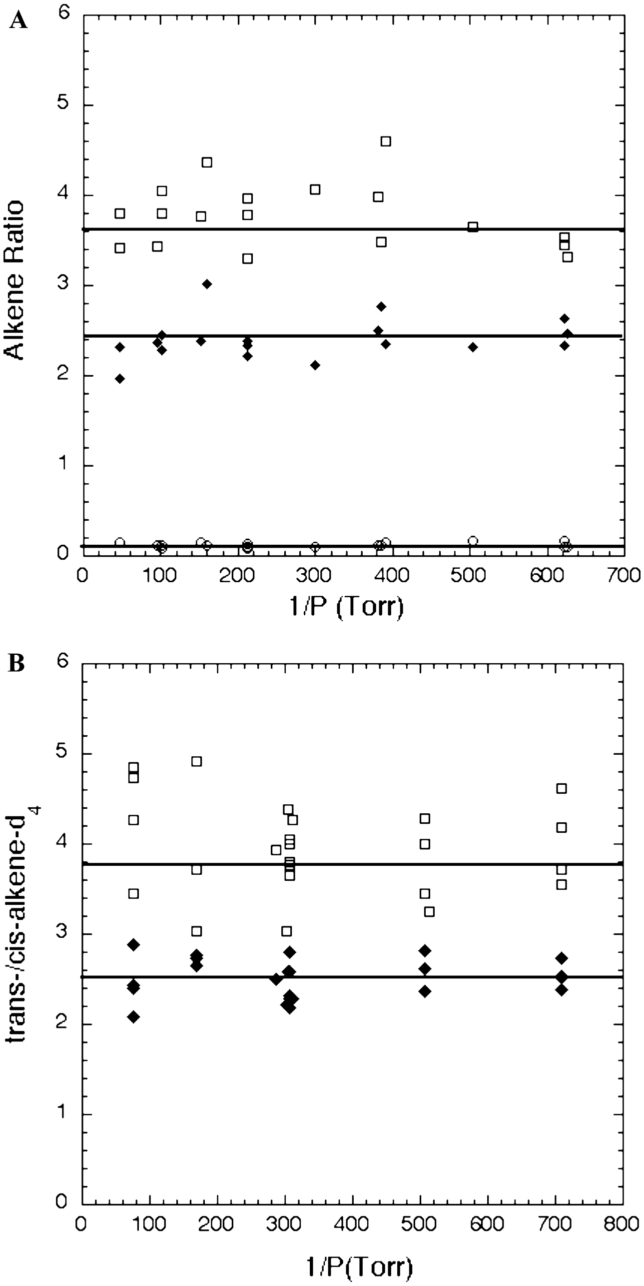

Figure 3. (A) Plots of product ratios vs pressure^{-1} for $CF_2ClCHFC_2H_5$: *trans*-$CF_2ClCH{=}CHCH_3$/*cis*-$CF_2ClCH{=}CHCH_3$ (□), *trans*-$CF_3CH{=}CHCH_3$/*cis*-$CF_3CH{=}CHCH_3$ (◆), and $CF_2{=}CHC_2H_5$/*trans*-$CF_3CH{=}CHCH_3$ (○). All data are from GC−mass spectrometric measurements, and the ratios are those of the most abundant ion. (B) Plots of product ratios vs pressure^{-1} for $CF_2ClCHFC_2D_5$: *trans*-$CF_2ClCH{=}CDCD_3$/*cis*-$CF_2ClCH{=}CDCD_3$ (□) *trans*-$CF_3CH{=}CDCD_3$/*cis*-$CF_3CH{=}CDCD_3$ (◆). All data are from GC−mass spectrometric measurements.

Several assumptions about the response factors of the flame-ionization and mass-spectrometric detectors were made to construct the D_i/S and olefin product branching ratios vs pressure^{-1} plots. Thus, the total uncertainty in the rate constants is larger than the standard deviations listed from the slopes of the D_i/S plots in Table 2. One check on the rate constants is the kinetic-isotope effects, which must be reasonable based on results from similar molecules.[1,4,5] The kinetic-isotope effects are 3.5 for 2,3-HF(DF) elimination and 2.1 for 1,2-ClF interchange. The latter is a pure secondary statistical effect and should be smaller than for HF(DF) elimination. The data for $CF_2ClCHFC_2H_5$ and $CF_2ClCHFC_2D_5$ seem self-consistent, although the kinetic-isotope effects are slightly low, *vide infra*.

The rate constants in Torr units were converted to s^{-1} with the collision constant, k_M. The collision diameters and ϵ/k values[20,21] used to obtain k_M units are given in the footnotes of Table 2. The uncertainty in the collision cross sections augments the experimental uncertainty in the rate constants derived from the slopes of the D_i/S plots. This uncertainty, plus assumptions for calibration of the detectors, suggested the ±20% uncertainty that is listed for rate constants in s^{-1}. In fact, the uncertainty may be larger especially for the 1,2-ClH and 2,3-ClH(ClD) processes. The intrinsic uncertainties associated with chemical activation rate constants reported for fluorochloropropanes were summarized in refs 4 and 6.

4.2. Thermochemistry. In order to assign E_0 values from experimental rate constants, the average vibrational energies of $CF_2ClCHFC_2H_5(C_2D_5)$ and $CF_3CHClC_2H_5(C_2D_5)$ must be known. The average vibrational energy for molecules formed by radical recombination with zero activation energy can be obtained from eq 11. The 3*RT* arises from the 3 translational and 3 rotational

$$\langle E(CF_2ClCHFC_2H_5)\rangle = D_0(CF_2ClCHF{-}C_2H_5) + 3RT + \langle E_V(C_2H_5)\rangle + \langle E_V(CF_2ClCHF)\rangle \quad (11)$$

motions of the radicals that become vibrational motions in the molecule. The $\langle E_V(C_2H_5)\rangle$ and $\langle E_V(CF_2ClCHF)\rangle$ terms are the average vibrational energy of the radicals at 298 K. The most important term is the bond-dissociation energy, which is obtained from enthalpies of formation. The $\Delta H°_{f,298}(C_2H_5)$ is established (28.9 kcal mol^{-1}),[22] and we previously used[1] isodesmic reactions to find $\Delta H°_{f,298}(CF_2ClCHF) = -118$ kcal mol^{-1}. The following isodesmic reactions were employed to estimate $\Delta H°_f(CF_2ClCHFC_2H_5)$.

$$CF_2ClCHFCH_3 + C_2H_6 \rightarrow CF_2ClCHFC_2H_5 + CH_4 \quad (12)$$

$$\Delta H°_o = -2.0 \pm 0.3 \text{ kcal mol}^{-1}$$

$$CF_3CHFC_2H_5 + CH_3Cl \rightarrow CF_2ClCHFC_2H_5 + CH_3F \quad (13)$$

$$\Delta H°_o = 16.4 \pm 2.0 \text{ kcal mol}^{-1}$$

The average of the energy difference calculated for each reaction from HF/6-311+G(2d,p), B3PW91/6-31G(d′,p′), and B3PW91/6-311+G(2d,p) is indicated; the energies were calculated for the most stable conformers. The calculated energy change for each reaction is combined with experimental enthalpies of formation to obtain $\Delta H°_{f,298}(CF_2ClCHFC_2H_5)$. Reaction 12 depends upon our previously assigned $\Delta H°_f(CF_2ClCHFCH_3)$.[1] Reaction 13 uses the $\Delta H°_o(CF_3CHFC_2H_5)$ from ref 23; the other enthalpy values are from standard sources.[24,25] Combining the $\Delta H°_{f,298}$ values with $\Delta H°_o$ gives $\Delta H°_{f,298}(CF_2ClCHFC_2H_5) = -179.8$ and -181.6 kcal mol^{-1} for reactions 12 and 13, respectively. Combining the average value with $\Delta H°_f(C_2H_5)$ and $\Delta H°_f(CF_2ClCHF)$ gives $D_{298}(CF_2ClCHF{-}C_2H_5) = 91.4$ kcal mol^{-1}. This can be compared to $D_{298}(CF_2ClCHF{-}CH_3) = 92.1$ kcal mol^{-1}. The latter should be somewhat larger, and by weighting the result from reaction 12 more heavily, $D_{298}(CF_2ClCHF{-}C_2H_5) = 91.0$ kcal mol^{-1} was selected. Converting D_{298} to 0 K and adding the thermal energies gives $\langle E(CF_2ClCHFC_2H_5)\rangle = 93$ kcal mol^{-1}. The estimated uncertainty in this value is ±3 kcal mol^{-1}, and the complication associated with 9 conformers of $CF_2ClCHFC_2H_5$ must be remembered. The $\langle E(CF_2ClCHFC_2D_5)\rangle$ increases by 1 kcal mol^{-1} to 94 kcal mol^{-1}.

The difference in energy between $CF_3CHClC_2H_5$ and $CF_2ClCHFC_2H_5$, which is equivalent to the enthalpy for reaction

TABLE 2: Summary of Experimental Rate Constants[a,b]

	$CF_2ClCHFCH_2CH_3$		$CF_2ClCHFCD_2CD_3$	
reaction	(10^{-3}) Torr	s^{-1}	(10^{-3}) Torr	s^{-1}
2,3-FH(FD)	1.40 ± 0.06[c]	$2.1 \pm 0.4 \times 10^4$	0.40 ± 0.02[c]	$0.60 \pm 0.12 \times 10^4$
1,2-ClF	0.88 ± 0.05[d]	$1.3 \pm 0.2 \times 10^4$	0.42 ± 0.03[d]	$0.63 \pm 0.12 \times 10^4$
1,2-ClH	0.20 ± 0.06	$0.29 \pm 0.10 \times 10^4$	not assigned[e]	
1,2-FH	not observed[f]		not observed[f]	
	$CF_3CHClCH_2CH_3$		$CF_3CHClCD_2CD_3$	
2,3-ClH(ClD)	116 ± 6[b,d]	$1.8 \pm 0.3 \times 10^6$	32.7 ± 2.5[d]	$0.49 \pm 0.09 \times 10^6$
1,2-FH	not observed[f]		not observed[f]	

[a] The listed uncertainties in the rate constants in Torr units are the standard deviations from the D_i/S vs pressure^{-1} plots. The absolute uncertainty in the unimolecular rate constants in s^{-1} units is considerably larger because of uncertainties in calibration of the response of the gas chromatograph and in the collision cross sections. Thus, the uncertainties were increased to ±20% for the rate constants in s^{-1} units. [b] The rate constants in Torr units were converted to s^{-1} using the following collision diameters and ϵ/K values:[19,20] $CF_2ClCHFC_2H_5$ (5.5 Å and 410 K); $CF_3CHClC_2H_5$ (5.5 Å and 410 K); $CF_2ClCHFI$ (5.2 Å and 400 K); C_2H_5I (5.0 Å and 405 K); $k_M = \pi d^2_{AM}(8kT/\pi\mu_{AM})^{1/2}\Omega^{2,2}(T^*)$. [c] The ratio of *trans*- to *cis*-$CF_2ClCH{=}CHCH_3$ was 3.7. [d] The ratio of *trans*- to *cis*-$CF_3CH{=}CHCH_3$ was 2.4. [e] The yield of $CF_2{=}CHC_2D_5$ was observed, but it was too small to be measured reliably because the overall extent of decomposition of $CF_2ClCHFC_2D_5$ was low, see Figures 1 and 4. [f] 1,2-FH elimination from $CF_2ClCHFC_2H_5$ or $CF_2CHClC_2H_5$ was not observed; therefore, the rate constant must be ≤2−3 times that for 1,2-ClH elimination.

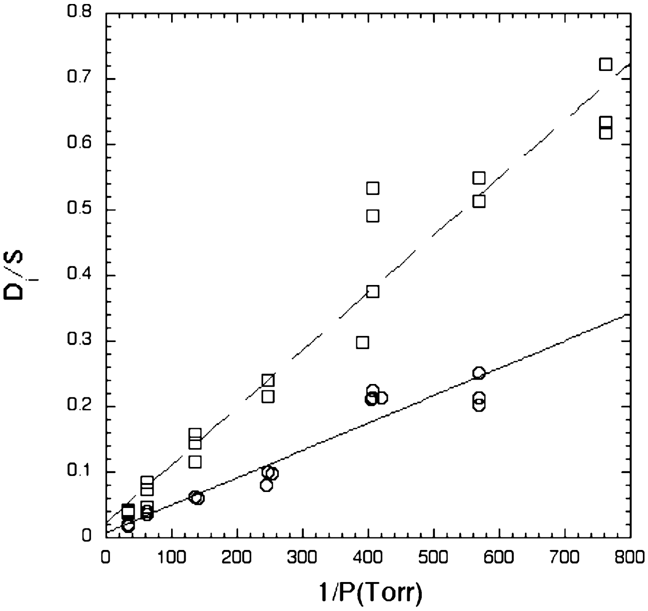

Figure 4. Plots of D/S ratio vs pressure^{-1} for 1,2-ClF interchange for S = $CF_2ClCHFC_2H_5$ (□) and $CF_2ClCHFC_2D_5$ (○). The D_i includes all decomposition products; *trans*- and *cis*-$CF_3CH{=}CHCH_3$ plus $CF_3CHClC_2H_5$ for (□) and *trans*- and *cis*-$CF_3CH{=}CDCD_3$ plus $CF_3CHClC_2D_5$ for (○). The slope is $(0.88 \pm 0.05) \times 10^{-3}$ Torr and the intercept is 0.024 ± 0.019 with a correlation coefficient of 0.97 for $CF_2ClCHFC_2H_5$, and for $CF_2ClCHFC_2D_5$ the slope is $(0.42 \pm 0.03) \times 10^{-3}$ Torr, the intercept is 0.009 ± 0.009, and the correlation coefficient is 0.96.

3, was calculated from two basis sets for the lowest energy conformers. The values were 12.1 and 9.7 kcal mol^{-1} for the G-31G(d′,p′) and 6-311+G(2d,p) basis sets, respectively. These values are similar to the corresponding values (−12.4 and −9.5 kcal mol^{-1}) for the $CF_2ClCHFCH_3$ to $CF_3CHClCH_3$ interchange reaction. We used an average of −11 kcal mol^{-1} for the enthalpy change of reaction 3.

In order to compare the reactions of $CF_2ClCHFC_2H_5$ with $CH_3CHFC_2H_5$, the average energy of 2-fluorobutane[11] formed by recombination of CH_3CHF and C_2H_5 radicals at room temperature is needed. Since $\Delta H^\circ_{f,298}(C_2H_5)$[22] and $\Delta H^\circ_{f,298}(CH_3CHF)$[26] are established as 28.9 and −18.2 kcal mol^{-1}, an estimate for $\Delta H^\circ_{f,298}(CH_3CHFC_2H_5)$ is needed to use eq 11. A recent comprehensive summary[23] of the enthalpies of formation of fluorinated alkanes gives $\Delta H^\circ_{f,298}(CH_3CHFC_2H_5)$ as −79.1 kcal mol^{-1}. Another approach to $\Delta H^\circ_{f,298}(CH_3CHFC_2H_5)$ is to use the established C−F bond dissociation enthalpy value for CH_3CHFCH_3[23,26] of 117 kcal mol^{-1} and to assume the same value for 2-fluorobutane. With this assumption and with enthalpies of formation[27] of 2-propyl and 2-butyl radicals, the $\Delta H^\circ_{f,298}(CH_3CHFC_2H_5)$ is −82.0 kcal mol^{-1}, which supports the values of ref 23. For these enthalpies of formation, the ΔH°_{298} for recombination of CH_3CHF and C_2H_5 is −89.8 kcal mol^{-1}. Application of eq 11 gives $\langle E(CH_3CHFC_2H_5\rangle = 92$ kcal mol^{-1} for radical recombination at room temperature. The reaction of CH_2 with CH_3CHFCH_3 at 300 K also has been used to prepare vibrationally excited $CH_3CHFC_2H_5$ molecules.[11] The enthalpies of formation for CH_2,[26] CH_3CHFCH_3,[24] and $CH_3CHFC_2H_5$[23] plus the thermal energy give $\langle E(CH_3CHFC_2H_5)\rangle = 107$ kcal mol^{-1}.

4.3. Assignment of Threshold Energies. *4.3.a. 2,3-FH and 2,3-ClH Elimination Reactions.* The torsional motion of the CH_3 group of the C_2H_5 fragment was treated as a vibration both in the molecule and in the transition states, because the sum-to-density ratio in eq 10 is insensitive as to whether vibrational or hindered internal rotational models are used, provided that the same model is used for the molecule and transition state. The frequencies for the nine conformers of the $CF_2ClCHFC_2H_5$ molecule and the three conformers of the $CF_3CHClC_2H_5$ molecule were averaged for the calculation of this density of states; details are provided in Table S1. Separate rate constant calculations were done for the *cis*- and *trans*-isomers of the transition states; however, only the lowest energy conformer associated with the CF_2Cl rotor was utilized for 2,3-FH elimination. The $CF_2ClCHF{-}C_2H_5$ and $CF_3CHCl{-}C_2H_5$ torsional motions of the molecules were treated as symmetric hindered rotors with $I_{red} = 22$ and 24 amu Å^2, respectively, with $V = 4.0$ kcal mol^{-1}. The $CF_2Cl(CF_3)$ torsion was treated as a hindered internal rotor with $I_{red} = 50$ (60) amu Å^2 and $V = 5.0$ (4.7) kcal mol^{-1}, respectively. These reduced moments were obtained as average values from the various conformers. The same potential barriers were used for the hindered rotors in the transition states; however, $I^{\ddagger}_{red}$ was calculated for each transition state.

A full description of the 9 conformers of $CF_2ClCHFC_2H_5$ is provided in the Supporting Information, and we will only give a summary. The lowest energy conformer has *trans*-configurations for the Cl and CH_2CH_3 groups (CF_2Cl rotor) and for the CH_3 and CF_2Cl groups (CH_2CH_3 rotor). Rotation of the CF_2Cl group for the fixed most stable configuration of C_2H_5 gives two more conformers, which differ in energy by ≤0.5 kcal mol^{-1}. Rotation of the CH_2CH_3 group for the most stable CF_2Cl configuration gives two higher (1.2 and 1.3 kcal mol^{-1}) energy

TABLE 3: Comparison of Calculated and Experimental Rate Constants

reaction	k_a(exp) s^{-1}	$\langle E\rangle^a$ kcal/mol	$k_{\langle E\rangle}{}^a$ s^{-1}	$E_0{}^b$ kcal/mol
$CF_2ClCHFC_2H_5$				
2,3-FH (*cis*)	$(0.45 \pm 0.10) \times 10^4$	93−95	$(0.52-0.92) \times 10^4$	63
2,3-FH (*trans*)	$(1.6 \pm 0.3) \times 10^4$		$(1.5-2.6) \times 10^4$	61
Cl−F interchange	$(1.3 \pm 0.2) \times 10^4$	93−95	$(1.3-2.6) \times 10^4$	60
1,2-ClH	$(0.29 \pm 0.10) \times 10^4$	93−95	$(0.32-0.59) \times 10^4$	65
1,2-FH	not observed			$\geq 68^d$
$CF_2ClCHFC_2D_5$				
2,3-FD (*cis*)	$(0.12 \pm 0.02) \times 10^4$	94−96	$(0.086-0.16) \times 10^4$	64
2,3-FD (*trans*)	$(0.48 \pm 0.10) \times 10^4$		$(0.29-0.51) \times 10^4$	62
ClF-interchange	$(0.63 \pm 0.12) \times 10^4$	94−96	$(0.38-0.63) \times 10^4$	60
1,2-ClH	not assigned	94−96		≈ 65
1,2-FH	not observed			$\geq 68^d$
$CF_3CHClC_2H_5$				
2,3-ClH (*cis*)	$(0.53 \pm 0.3) \times 10^6$	104−106	$(0.48-0.72) \times 10^6$	61
2,3-ClH (*trans*)	$(1.3 \pm 0.2) \times 10^6$		$(1.2-1.7) \times 10^6$	59
Cl−F interchange	$(0.35 \times 10^4)^c$	104−106		$(71)^c$
1,2-FH	not observed			$\geq 79^d$
$CF_3CHClC_2D_5$				
2,3-ClD (*cis*)	$(0.14 \pm 0.03) \times 10^6$	105−107	$(0.14-0.21) \times 10^6$	62
2,3-ClD (*trans*)	$(0.35 \pm 0.06) \times 10^6$		$(0.34-0.50) \times 10^6$	60
Cl−F interchange	$(0.16 \times 10^4)^c$	105−107		$(71)^d$
1,2-FH	not observed			$\geq 79^d$

[a] The two $k_{\langle E\rangle}$ values correspond to $\langle E\rangle = 93$ and 95 kcal mol^{-1} for $CF_2ClCHFC_2H_5$ and 94 and 96 kcal mol^{-1} for $CF_2ClCHFC_2D_5$. A change in E_0 of 1 kcal mol^{-1} has roughly the same effect as a 2 kcal mol^{-1} change in $\langle E\rangle$. [b] Assigned by matching k_a(expt) and $k_{\langle E\rangle}$ for E equal to the average energy, $\langle E\rangle$, for $CF_2ClCHFC_2H_5$ and $CF_3CHClC_2H_5$. The E_0 values for $CF_2ClCHFC_2D_5$ were obtained from consideration of calculated zero-point energy changes and matching k_{expt}. The rate constants for $CF_2ClCHFC_2D_5$ were based on the density of states of the lowest energy conformer (see text). [c] The E_0 was assigned as E_0(ClF; $CF_2ClCHFC_2H_5$)$- \Delta H^\circ_R$. The rate constant was estimated from k(1,2-ClF) and the equilibrium constants for $CF_2ClCHFC_2H_5$ (C_2D_5) and $CF_3CHClC_2H_5$ (C_2D_5). [d] The E_0 for 1,2-FH elimination was estimated to be ≥ 3 kcal mol^{-1} larger than for 1,2-ClH elimination from $CF_2ClCHFC_2H_5$ and the E_0 for 1,2-FH elimination from $CF_3CHClC_2H_5$ would be 11 kcal mol^{-1} higher than for $CF_2ClCHFC_2H_5$.

conformers. The four remaining conformers have relative energies of 1.3, 1.6, 2.6, and 2.8 kcal mol^{-1}. In summary, the difference in energies of the conformers is ≤ 2.8 kcal mol^{-1}. Relative to the most stable conformer, the energy barriers for rotation of the CF_2Cl group were 4.1, 5.7, and 4.6 kcal mol^{-1}; the barriers for rotation of the CH_2CH_3 group were 3.0, 6.2, and 3.7 kcal mol^{-1}. The symmetric internal rotor approximation will be least satisfactory for the C_2H_5 internal rotation. The lowest energy conformer for $CF_3CHClC_2H_5$ has the CH_3 and CF_3 in *trans* position; the other two conformers are 1.0 and 1.2 kcal mol^{-1} higher in energy.

Rate constants for the *cis*- and *trans*-pathways were calculated as a function of energy for several values of the threshold energy, and then E_0 values were selected to give the best match with k_{expt} values as shown in Table 3. Since the assignment of $\langle E\rangle$ is not very precise, calculated rate constants are given for 93 and 95 kcal^{-1}. The rate constants are quite sensitive to both $\langle E\rangle$ and E_0; a 2 kcal mol^{-1} increase in $\langle E\rangle$, which is equivalent to a 1 kcal mol^{-1} decrease in E_0, increases the rate constants by a factor of $\approx$1.6. The assigned values for 2,3-FH elimination from $CF_2ClCHFC_2H_5$ are 61 and 63 kcal mol^{-1}, for the *trans*- and *cis*-channels, respectively. The assigned E_0 values for 2,3-ClH elimination from $CF_3CHClC_2H_5$ are 59 and 61 kcal mol^{-1} for the *trans*- and *cis*-channels, respectively. The rate constant for $CF_3CHClC_2H_5$ is 80-fold larger than for $CF_2ClCHFC_2H_5$, because the $\langle E\rangle$ is 11 kcal mol^{-1} higher and the E_0(2,3-ClH) is lower than for 2,3-FH elimination from $CF_2ClCHFC_2H_5$.

Calculations for $CF_3CHClC_2D_5$ were done as the average of three conformers as described for $CF_3CHClC_2H_5$. However, the $CF_2ClCHFC_2D_5$ rate constant was calculated from properties of just the lowest energy conformer, rather than the average of 9 conformers. The assignments for E_0(2,3-FD) and E_0(2,3-ClD) listed in Table 3 are 1 kcal mol^{-1} higher than those for FH and ClH elimination, as expected from zero-point energy considerations. The primary isotope effect[1,4,5] on threshold energies for HX vs DX elimination is always about 1 kcal mol^{-1}. The statistical effect of the other 4 deuterium atoms augments the consequence of the higher threshold energy to obtain a calculated kinetic-isotope effect of 5.2 and 3.4 for $CF_2ClCHFC_2D_5$ and $CF_3CHClC_2D_5$, respectively. The calculated ratios include the 1.0 kcal mol^{-1} higher energy for $CF_2ClCHFC_2D_5$ and $CF_3CHClC_2D_5$. The use of the single conformer for $CF_2ClCHFC_2D_5$ in the calculation of N_E* is mainly responsible for the high value (5.2) for this isotope effect. If the lowest energy conformers are used for both $CF_2ClCHFC_2H_5$ and $CF_2ClCHFC_2D_5$, the calculated rate constant ratio would be 4.3. The experimental isotope ratios are 3.5 ± 0.3 and 3.6 ± 0.6. The data for $CF_2ClCHFC_2D_5$ do favor an E_0 (2,3-FH) elimination (trans) of about 61 kcal mol^{-1}. These intermolecular kinetic-isotope effects can be compared to HCl (DCl) elimination at $\langle E\rangle = 91$ kcal mol^{-1} from $C_2H_5CH_2Cl$ and $C_2D_5CH_2Cl$, which gave 4.0 and 3.8 for the experimental and calculated kinetic isotope effect, respectively.[4] The purpose of the $CF_2ClCHFC_2D_5$ experiments was to provide support for the interpretations of $CF_2ClCHFC_2H_5$ and to help identify products for which authentic samples were not available.

4.3.b. 1,2-ClF Interchange and 1,2-ClH Elimination Reactions. The same model for the molecule as described in section 4.3.a was used for these rate constant calculations. The C_2H_5 torsion was treated as a hindered rotor, and the frequencies of lowest energy conformers of both transition states were used for the rate constant calculations. The average $I^{\ddagger}_{red}(C_2H_5)$ were 23.8 and 25.0 amu Å^2 for the ClF and ClH transition states with V selected as 4 kcal mol^{-1}. The reaction path degeneracy is unity for both channels. The assigned threshold energies listed in Table 3 are 60 and 65 kcal mol^{-1} for 1,2-ClF interchange and 1,2-ClH elimination, respectively. The threshold energy for 1,2-ClF interchange definitely seems to be the lowest of the three reactions for $CF_2ClCHFC_2H_5$. Given the large uncertainty in k_{expt}(1,2-ClH), the threshold energy for 1,2-ClH elimination has a 2−3 kcal mol^{-1} uncertainty.

The kinetic-isotope effect for 1,2-ClF interchange from $CF_2ClCHFC_2D_5$ is a pure statistical effect, and the threshold energy should not be affected, which was confirmed by examining changes in the zero-point energies. The calculated rate constant for $CF_2ClCHFC_2D_5$ with $\langle E \rangle$ one kcal mol^{-1} higher, but with the same threshold energy as for $CF_2ClCHFC_2H_5$, is listed in Table 3. The calculated rate constant for $CF_2ClCHFC_2D_5$ is somewhat lower than the experimental value. Stated another way, the experimental kinetic-isotope effect is 2.1 ± 0.2, whereas the calculated rate constant ratio for 1,2-ClF rearrangement with a one kcal mol^{-1} difference in $\langle E \rangle$ is 3.3. Part of this discrepancy is a consequence of basing the $CF_2ClCHFC_2D_5$ calculation on just the lowest energy conformer. According to the $CF_2ClCHFC_2H_5$ calculations, the density of states for $CF_2ClCHFC_2D_5$ would be lower by a factor of 0.81 for the average of all nine conformers, and the kinetic isotope effect would be 2.7. The low fractional conversion to decomposition products for $CF_2ClCHFC_2D_5$ also makes these data less reliable. Nevertheless, the $CF_2ClCHFC_2D_5$ data support an E_0(ClF) of 60 ± 2 kcal mol^{-1}. The rate constant for 1,2-ClH elimination from $CF_2ClCHFC_2D_5$ could not be measured, because the yield of $CF_2{=}CHC_2D_5$ was too low.

5. Discussion

5.1. Comparison of $CF_2ClCHFC_2H_5$ with $CF_2ClCHFCH_3$. The pattern for the rate constants of $CF_2ClCHFC_2H_5$ and $CF_2ClCHFCH_3$[1] is very similar with $k_{2,3-FH} \geq k_{1,2-ClF} > k_{1,2-ClH}$, and $CF_2ClCHFC_2H_5(C_2D_5)$ provides another example for which 1,2-ClF interchange is important. Changing a CH_3 group to a C_2H_5 group did not strongly affect the branching ratios. However, the rate constants for $CF_2ClCHFC_2H_5$ are 115−150 times smaller than for $CF_2ClCHFCH_3$. RRKM calculations for the same threshold energies predict a reduction in rate constants by a factor of 30 for $CF_2ClCHFC_2H_5$ relative to $CF_2ClCHFCH_3$. Thus, ≈2 kcal mol^{-1} higher values of E_0, relative to $CF_2ClCHFCH_3$, were required to fit the k_{expt} values of $CF_2ClCHFC_2H_5$; the E_0 (*trans*-2,3-FH) was used in this comparison. The main question to be answered is whether the difference in assigned threshold energies between $CF_2ClCHFCH_3$ and $CF_2ClCHFC_2H_5$ is real or a consequence of the combined uncertainties in k_{expt} and the calculated $k_{\langle E \rangle}$. An additional piece of evidence is the DFT calculated threshold energies for the three unimolecular pathways for both molecules. The threshold energies from the B3PW91/6-31G(d′,p′) calculations for $CF_2ClCHFC_2H_5$ were 56.2, 59.7, and 56.0 kcal mol^{-1}, for Cl−F interchange, 2,3-FH elimination (*trans*-channel), and 1,2-ClH elimination, respectively, for the lowest energy conformers of the molecule and transition state. These values are virtually identical to those calculated for $CF_2ClCHFCH_3$.[1] Based on these DFT calculations and upon general expectations for substitution of a CH_3 group by a C_2H_5 group, we believe that the higher threshold energies assigned to the $CF_2ClCHFC_2H_5$ data are a consequence of the combined uncertainties associated with the experimental data and the computational models (including the $\langle E \rangle$). For example, if the density of states is underestimated by a factor of 2, the calculated rate constants would be too large by a factor of 2, which requires a higher E_0 to reduce the rate constant. In particular, the large number of conformers for the $CF_2ClCHFC_2H_5$ molecule, as well as 2−3 conformers or isomers for each transition state, make the assignment of an average E_0 for each channel somewhat arbitrary. The pressures for experiments with $CF_2ClCHFC_2H_5$ were in the range of 0.02 to 0.002 Torr. If the residual pressure in the nominally empty vessels was higher than measured on the vacuum line, the pressures calculated from the measured samples placed in the vessels could have been underestimated especially for low-pressure experiments in large vessels. As a final point, the high value assigned to E_0(1,2-ClH) for $CF_2ClCHFC_2H_5$ fits the trend found for $CF_2ClCHFCH_3$, e.g., the discrepancy between the DFT calculated threshold energy and the much higher value assigned from experimental data exists for both molecules. Since the product branching fraction for 1,2-ClH elimination is very low, a high E_0(1,2-ClH) seems definitely required.

The reduction of the 2,3-ClH rate constant for $CF_3CHClC_2H_5$ vs $CF_3CHClCH_3$ is only a factor of 31, and the ratio for $CF_3CHClC_2D_5$ vs $CF_3CHClCD_3$ is 46. These smaller ratios are partly a consequence of the higher energy of the molecule with a correspondingly larger $\langle E \rangle - E_0$(2,3-ClH); the calculated ratio is about 20 rather than 30 for $CF_2ClCHFC_2H_5$. Agreement between the experimental and calculated rate constants for $CF_3CHClC_2H_5$ was obtained with only a 1−2 kcal mol^{-1} increase in E_0(1,2-ClH) relative to $CF_3CHClCH_3$. This closer match is probably fortuitous, since the data for 2,3-ClH elimination have more uncertainty than the data upon which the rate constants for $CF_2ClCHFC_2H_5$ are based.

5.2. Comparison of $CF_2ClCHFC_2H_5$ with $CH_3CHFC_2H_5$. The HF elimination reactions of $CH_3CHFC_2H_5$ formed by combination of C_2H_5 and CH_3CHF radicals were studied in 1973 as part of a comprehensive program to characterize unimolecular HX elimination reactions.[11] These data can be reinterpreted using our current computational approach to provide another link[28] to earlier work and to elucidate the differences between CH_3 and CF_2Cl groups on the threshold energies for 2,3-FH elimination. The experimental rate constants for $CH_3CHFC_2H_5$ with $\langle E \rangle = 92$ kcal mol^{-1} were 0.20 Torr (3.6×10^6 s^{-1}) and 0.26 Torr (4.7×10^6 s^{-1}) for 2,3-FH and 2,1-FH elimination, respectively.[11]

In order to interpret the $CH_3CHFC_2H_5$ system, DFT calculations with the 6-31G(d′,p′) basis set were done for the molecule and for the transition states of $CH_3CHFC_2H_5$, and then RRKM calculations were done for 2,1-FH and 2,3-FH reactions. The three conformers of $CH_3CHFC_2H_5$ have similar energies and vibrational frequencies,[14] and we used the average frequencies of the three conformers to represent the molecule. For the 2,3-FH reaction, the $-C_2H_5$ torsion was treated as a symmetric hindered rotor with a barrier height[3] of 4.6 kcal mol^{-1} with $I_{red} = 15.5$ amu Å^2. The torsional motions of the two CH_3 groups were treated as vibrations, since these modes are the same for the molecule and the transition state. Rate constants for the *cis*- and *trans*-isomers were added to obtain the total rate constant for butene-2 formation. The E_0 required to match the experimental 2,3-FH rate constant is 54 kcal mol^{-1}. Calculations were extended to include the 2,3-FH reaction from $CH_3CHFC_2H_5$ formed with 107 kcal mol^{-1} from the $CH_2(\tilde{a}) + CH_3CHFCH_3$ reaction,[11] which has an experimental rate constant 15 times larger than the rate constant for molecules formed by radical recombination.[29] The calculated increase in k(2,3-FH) was a factor of 10. This modest agreement with the experimental ratio is satisfactory given the possibilities of (a) cascade collisional deactivation of $CH_3CH_2FC_2H_5$ which would tend to increase the experimental rate constant, and (b) additional energy from vibrational excitation of the bending mode of CH_2 from the photolysis.[30]

The rate constant for 2,1-FH elimination also was fitted by RRKM calculations. In this case the C_2H_5 group has similar modes in the molecule and transition state, and the torsional

TABLE 4: Comparison of 2,3-XH Elimination Reactions

molecule	reference	$\langle E \rangle$ kcal/mol	k_{expt}, s^{-1}	assigned E_0 kcal/mol
$CF_2ClCHFC_2H_5$	this work	93	2.1×10^4	62
$CF_2ClCHFCH_3$	1	94.3	3.1×10^6	59.5
$CF_3CHClC_2H_5$	this work	104	1.8×10^6	60
$CF_3CHClCH_3$	1	105.2	5.5×10^7	59.0
CF_3CHFCH_3	6	97.0	3.7×10^6	60.5
CH_3CHFCH_3[a]	4	95	1.1×10^8	55
$CH_3CHFC_2H_5$[b]	11; this work	92	3.6×10^6	54

[a] The rate constant for one methyl group of CH_3CHFCH_3 was inferred from that of CD_3CHFCH_3, ref 4; see ref 30 for thermal activation data. [b] The 1,2-HF elimination rate constant was approximately equal to the 2,3-FH rate constant, and the threshold energy is 53 kcal mol^{-1}; see text.

motions of the C_2H_5 group were treated as vibrations. However, the $CH_3-CHFC_2H_5$ torsion in the molecule was treated as a hindered rotor with $I_{red} = 3.08$ amu Å^2 and $V = 3.0$ kcal mol^{-1}. The frequencies of the other modes were taken as the average of the conformers. The assigned E_0(1,2-HF) was 53 kcal mol^{-1}, and the difference in the threshold energies between elimination of HF from a primary vs a secondary C−H bond is negligible in $CH_3CHFC_2H_5$. The assigned threshold energies for $CH_3CHFC_2H_5$ are in accord with thermal activation experiments with CH_3CHFCH_3[31a] and $CH_3CHClCH_3$.[31b] The E_0 values assigned here for $CH_3CHFCH_2CH_3$ are the same as those in ref 11. Although the transition states from DFT calculations have a higher entropy than the empirical transition states used earlier, the utilization of hindered internal rotors in the model for the molecule leads to the same $(\sum P^{\ddagger}(E - E_0)/N_E^*$ ratio.[4,28]

Several 2,3-FH elimination rate constants are compared in Table 4 for molecules with ≈95 kcal mol^{-1} of energy. The reduced rate constants of CF_3CHFCH_3 and $CF_2ClCHFCH_3$, relative to CH_3CHFCH_3, illustrate the effect of the F and Cl atoms in CF_3 or CF_2Cl groups, which increase the density of states *and* raise the threshold energy by 5 kcal mol^{-1}. The reduction in rate constant for converting a CH_3 group in $CH_3CHFC_2H_5$ to CF_2Cl in $CF_2ClCHFC_2H_5$ also is 2 orders of magnitude. As an explanation for the elevation in E_0 by CF_3 or CF_2Cl groups, we compared $D(CF_3-CH{=}CH_2)$ and $D(CF_3-CH_2CH_3)$ vs $D(CH_3-CH{=}CH_2)$ and $D(CH_3-CH_2CH_3)$.

$$D(CF_3-CH{=}CH_2) - D(CF_3-CH_2CH_3) = 106.7 - 102.1 = 4.6 \text{ kcal mol}^{-1}$$

$$D(CH_3-CH{=}CH_2) - D(CH_3-CH_2CH_3) = 101.7 - 88.0 = 13.7 \text{ kcal mol}^{-1} \quad (14)$$

The calculated transition-state structures[1−6] for HF elimination have a high degree of olefinic character, and the bond dissociation energies for $CF_3CH{=}CH_2$ and $CH_3CH{=}CH_2$ were chosen to represent the transition state. The CF_3−C bond strength does not increase nearly as much for trifluoropropene as does the CH_3−C bond strength in propene. Given the olefinic nature of the carbon atoms in the four-membered ring of the transition state, this has the net effect of increasing the threshold energy for HF elimination from compounds with a CF_3 group rather than a CH_3 group on carbon atoms in the four-membered ring. The analogy can be extended to 2,3-HCl elimination from $CH_3CH_2CH_2Cl$ and $CF_3CH_2CH_2Cl$; the latter has a 4 kcal mol^{-1} higher E_0.[4]

It has long been recognized[32,33] that replacement of H by CH_3 on the carbons in the ring lowered the E_0 for the 1,2-HX elimination reaction. This was attributed to the methyl group dispersing the partial charges that developed on the carbons in the ring rather than the effect of changes in bond strengths for sp^3 hybridized carbons versus carbons with significant olefinic character. To test whether the electronic structural calculations would support the explanation based on dispersal of partial charges for an ionic transition state, Mulliken charges for the individual atoms were calculated using the B3LYP density at the optimized geometry in each molecule ($CF_2ClCHFC_2H_5$, $CF_3CHClC_2H_5$, and $CH_3CHFC_2H_5$) and the lowest energy conformer for each transition state; see Table S1 in the Supporting Information. Results of an earlier[13,34] calculation for CF_3CH_3 regarding the redistribution of charge as the HF transition state forms is confirmed for HF elimination from all three halobutanes. Movement of electron density is largest to the departing X with Cl experiencing a greater gain in electron density than F. Examination of the charges on the $CH_3CHFCH_2CH_3$ and the 2,3-FH transition states in Table S1 illustrates the effect of a methyl substituent attached to each of the carbons in the ring. The Mulliken charges on the two methyl substituents are nearly identical for the reactant and for the *E* and *Z* transition states. In fact, the variation of electron density between different molecular rotomers is greater than the change when the transition state forms. This suggests that the methyl substituent on either the carbon with the departing F or the carbon with the departing H neither accepts nor donates electron density. This observation is counter to the explanation that methyl substituents donate electron density to stabilize the developing charge on the carbons in the ring of the transition state. Thus, we believe our view that differences in bond strengths for atoms attached to an sp^3 hybridized carbon versus a carbon with significant olefinic character might be responsible for the changes in E_0. Finally, dipole moments for the reactants and the transition states are also in Table S1. Due to the significant lengthening of the C−X bond in the transition state the dipole moments for all HX elimination transition states are larger than for the molecule. The increase in dipole moment is much larger for HCl loss than for HF.

5.3. Considerations of Product Branching Ratios from $CF_2ClCHFC_2H_5$. Although threshold energies are the dominant factors that determine product branching fractions, the structures of the three transition states and the approximations in our treatment of their internal rotors should be examined. Furthermore, the 2,3-XH processes have *cis*- and *trans*-isomers and the reason that the *trans*-isomer is favored needs to be explained. The *trans*-transition state has the $CF_2Cl(CF_3)$ and CH_3 groups on opposite sides of the nearly planar four-membered ring, and this transition state evolves naturally to *trans*-$CF_2ClCH{=}CHCH_3$ (or *trans*-$CF_3CH{=}CHCH_3$). The *cis*-transition states give *cis*-olefin products. At the same vibrational energy, the two transition states have nearly the same sums of states, and the preference for the *trans* product arises from the 2−3 kcal mol^{-1} lower energy of the *trans*-transition state (a 2 kcal mol^{-1} difference in E_0 gives a factor of 2.7 and 3 kcal mol^{-1} gives 4.5 in the rate constant). This energy difference is nearly the same as for the olefin products, which is additional confirmation that the transition states for HX-elimination have considerable olefinic character. The experimental *trans/cis* ratio of butene-2 from $CH_3CHFC_2H_5$ was only 1.2. The small ratio is a consequence of the small difference in threshold energies (1.0 kcal mol^{-1} from DFT calculations), as expected for the 1.0 kcal mol^{-1} difference in enthalpies of formation of *cis*- and *trans*-2-butene.

Comparison of the sums of states, $\sum P^{\pm}(E - E_0)$, for the three transition states of $CF_2ClCHFC_2H_5$ requires a consistent treatment for the torsional motions of CH_3, C_2H_5, and CF_2Cl groups.

We have treated the CH_3 torsion treated as a vibrational mode in all three transition states. For a common energy of 35 kcal mol^{-1} and for hindered internal rotational models for the CF_2Cl or C_2H_5 groups, the sums of states are 7.8×10^{14}, 24.1×10^{14}, and 15.1×10^{14} (*trans*) or 16.5×10^{14} (*cis*) for the transition states of 1,2-ClF, 1,2-ClH, and 2,3-FH reactions, respectively. As discussed previously[1-3] the transition state for ClF interchange has a rigid structure. After completing the calculations for 2-fluorobutane described above with only one hindered rotor in the molecule, we repeated the calculations with a two rotor model (the CH_3-CHF- rotor and the $-CHF-C_2H_5$ rotor). Thus, the 2,1-FH and 2,3-FH transition states can be more easily compared; the sums of states are 15.6×10^{11} and 9.4×10^{11} (*trans*-isomer), respectively. Thus, the C_2H_5 group provides more states than do two CH_3 groups. The rate constants calculated with the single rotor model for $CH_3CHFC_2H_5$ were virtually identical to those with the two rotor model, which verifies the assumptions made for the single rotor models which is much simpler.

Conclusions

The $CF_2ClCHFC_2H_5(C_2D_5)$ molecules with 93(94) kcal mol^{-1} of vibrational energy provide a third example of the 1,2-ClF interchange reaction. The other competing reactions are 2,3-FH(FD) elimination and 1,2-ClH elimination; the latter is the least important with a branching fraction of only 0.08 ± 0.04, and 1,2-FH elimination is completely negligible. The product of 1,2-ClF interchange, $CF_2ClCHFC_2H_5(C_2D_5)$, undergoes 2,3-ClH(ClD) elimination. For many chlorofluoroalkanes, the exchange of halogen atoms located on adjacent carbon atoms competes with other unimolecular channels.

The numerous conformers for the molecules and the transition states require choices to be made for models that can be used to obtain calculated RRKM rate constants. DFT calculations at the B3PW91/6-31G(d′,p′) level were done to obtain vibrational frequencies, moments of inertia, and barriers to internal rotation for the CF_2Cl (or CF_3 and CH_3) and C_2H_5 groups for all conformers of the three molecules. These results were then averaged to obtain a model for an average conformer. Since some conformers were difficult to define for transition states, we used the lowest energy conformers to calculate the sums of states for the transition states. Matching the calculated rate constant to the experimental values gave the threshold energies (for an average conformer) of 60 ± 2, 61 ± 2, and 65 ± 3 kcal mol^{-1} for ClF interchange, 2,3-FH elimination, and 1,2-ClH elimination, respectively. These values were supported by less extensive data for $CF_2ClCHFC_2D_5$. Although these threshold energies are ≈ 2 kcal mol^{-1} higher than those reported for $CF_2ClCHFCH_3$, the uncertainties in the data and the approximations made in the models for the calculations suggest that the threshold energies of the two molecules are nearly equivalent.

Previously published experimental data[11] for $CH_3CHFC_2H_5$ activated by recombination of CH_3CHF and C_2H_5 radicals at room temperature were fitted by RRKM calculations to obtain threshold energies of 53 and 54 kcal mol^{-1} for 1,2-HF and 2,3-FH elimination. The difference between a primary and secondary C−H bond in the four-centered ring, e.g., a $-CH_2-$ or $-CH_3$ group seems unimportant for HF elimination. However, the 2,3-FH threshold energy is 6−8 kcal mol^{-1} lower than that for $CF_2ClCHFC_2H_5$, and the CF_2Cl group increases the threshold energy for 2,3-FH elimination. Comparison of CH_3CHFCH_3 vs $CF_2ClCHFCH_3$ or CF_3CHFCH_3 and $CH_3CH_2CH_2Cl$ vs $CF_3CH_2CH_2Cl$ shows the same trend, which can be explained by the difference in bond energies of CF_3 and CH_3 groups in an alkane vs an alkene, and the olefinic nature of the transition states for HCl or HF elimination. Calculated Mulliken charges for the methyl substituents for the $CH_3CHFC_2H_5$ molecule and the 2,3-FH transition state do not support an earlier view[32,33] that replacement of H by a CH_3 substituent lowers the E_0 as a consequence of dispersal of the partial charges on the carbon atoms in the ring by the methyl group.

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Supporting Information Available: Dipole moments, Mulliken charges, calculated vibrational frequencies, and reduced moments of inertia and potential barriers. This material is available free of charge via the Internet at http://pubs.acs.org.

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