Unimolecular Reactions of $CF_2ClCFClCH_2F$ and $CF_2ClCF_2CH_2Cl$: Observation of ClF Interchange

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The unimolecular reactions of $CF_2ClCFClCH_2F$ and $CF_2ClCF_2CH_2Cl$ molecules formed with 87 and 91 kcal mol^{-1}, respectively, of vibrational energy from the recombination of $CF_2ClCFCl$ with CH_2F and CF_2ClCF_2 with CH_2Cl at room temperature have been studied by the chemical activation technique. The 2,3- and 1,2-ClF interchange reactions compete with 2,3-ClH and 2,3-FH elimination reactions. The total unimolecular rate constant for $CF_2ClCF_2CH_2Cl$ is $0.54 \pm 0.15 \times 10^4$ s^{-1} with branching fractions for 1,2-ClF interchange of 0.03 and 0.97 for 2,3-FH elimination. The total rate constant for $CF_2ClCFClCH_2F$ is $1.35 \pm 0.39 \times 10^4$ s^{-1} with branching fractions of 0.20 for 2,3-ClF interchange, 0.71 for 2,3-ClH elimination and 0.09 for 2,3-FH elimination; the products from 1,2-ClF interchange could be observed, but the rate constant was too small to be measured. The $D(CH_2F-CFClCF_2Cl)$ and $D(CH_2Cl-CF_2CF_2Cl)$ were evaluated by calculations for some isodesmic reactions and isomerization energies of $CF_3CFClCH_2Cl$ as 84 and 88 kcal mol^{-1}, respectively; these values give the average energies of formed molecules at 298 K as noted above. Density functional theory was used to assign vibrational frequencies and moments of inertia for the molecules and their transition states. These results were combined with statistical unimolecular reaction theory to assign threshold energies from the experimental rate constants for ClF interchange, ClH elimination and FH elimination. These assignments are compared with results from previous chemical activation experiments with $CF_3CFClCH_2Cl$, $CF_3CF_2CH_3$, $CF_3CFClCH_3$ and $CF_2ClCF_2CH_3$.

1. Introduction

Our laboratory has utilized the chemical activation technique to investigate halopropane molecules that exhibit unimolecular interchange of halogen atoms that are located on adjacent carbon atoms.[1−7] These interchange reactions are in close competition with HCl and HF elimination reactions. We have previously determined that the unimolecular decomposition pathways for chemically activated $CF_3CF_2CH_3$, $CF_3CFClCH_3$ and $CF_3CFClCH_2Cl$[1,2] involved 2,3-FH and 2,3-ClH elimination reactions; the ClF interchange reaction was not observed for the latter two molecules. The 100-fold reduction in the rate constants for $CF_3CFClCH_2Cl$ was explained[2] by a lower average energy, $\langle E \rangle$, higher threshold energy, E_0, and the change from a CH_3 internal rotation to a CH_2Cl internal rotation. The reduced $\langle E \rangle$, 87 versus 94−96 kcal mol^{-1}, is a direct consequence of the lower $D(CH_2Cl-CFClCF_3)$. The vibrationally excited $CF_3CFClCH_2Cl$ could react by either a 2,3- or 1,2-ClF interchange reaction but neither was observed. Our interest in the FCl interchange and HX (X = F, Cl) elimination reactions has been extended to include the $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$ isomeric molecules formed by the recombination of $CF_2ClCF_2 + CH_2Cl$ and $CF_2ClCFCl + CH_2F$ radicals at room temperature. In contrast with $CF_3CFClCH_2Cl$, 2,3-ClF interchange was a major reaction for $CF_2ClCFClCH_2F$ and 1,2-ClF interchange was a minor reaction for $CF_2ClCF_2CH_2Cl$ in competition with ClH and FH elimination. The numerous reaction channels are summarized for all three isomeric molecules in Figure 1.

The experimentally based threshold energies shown in Figure 1 for $CF_3CFClCH_2Cl$ were assigned in ref 2 and those for $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$ will be assigned in this work. The total unimolecular rate constants for these three molecules are small, and their $\langle E \rangle$ values must be similar, i.e., $D(CH_2F-CFClCF_2Cl)$ and $D(CH_2Cl-CF_2CF_2Cl)$ must resemble $D(CH_2Cl-CFClCF_3)$ more than $D(CH_3-CFClCF_3)$ or $D(CH_3-CF_2CF_3)$. The 1,2-ClF interchange process for $CF_2ClCF_2CH_2Cl$ also can be compared with interchange in $CF_2ClCF_2CH_3$.[3,4] These six fluoro- and fluorochloropropane molecules illustrate how small changes in structure can alter threshold energies and, hence, can influence rate constants of the competing unimolecular exit channels.

In our studies of the unimolecular reactions of the fluoro and fluorochloropropanes,[1−7] we have used density functional theory (DFT) to calculate the structures (vibrational frequencies and moments of inertia) of the molecules and their transition states. If a given structure had several conformers, the vibrational frequencies and moments of inertia were averaged because calculations of the RRKM rate constants were done with models that treated torsional motions as symmetric, hindered, internal rotations. The calculated RRKM rate constants were matched to the experimental rate constants by treating the threshold energy as a variable. This approach is laborious for $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$ because each molecule has 9 conformers, although $CF_2ClCF_2CH_2Cl$ has only 5 distinct conformers, and each transition state has 3 conformers. Two separate transition states were used to represent the 2,3-ClH and 2,3-FH reactions, because they proceed by pathways with *E*(trans) and *Z*(cis) geometry with respect to the positions of the two halogen atoms on the carbon atoms of the ring. To reduce the computational effort but still maintain a reasonable level of reliability,[7] the RRKM rate constant calculations were done with models based upon the structure of the average

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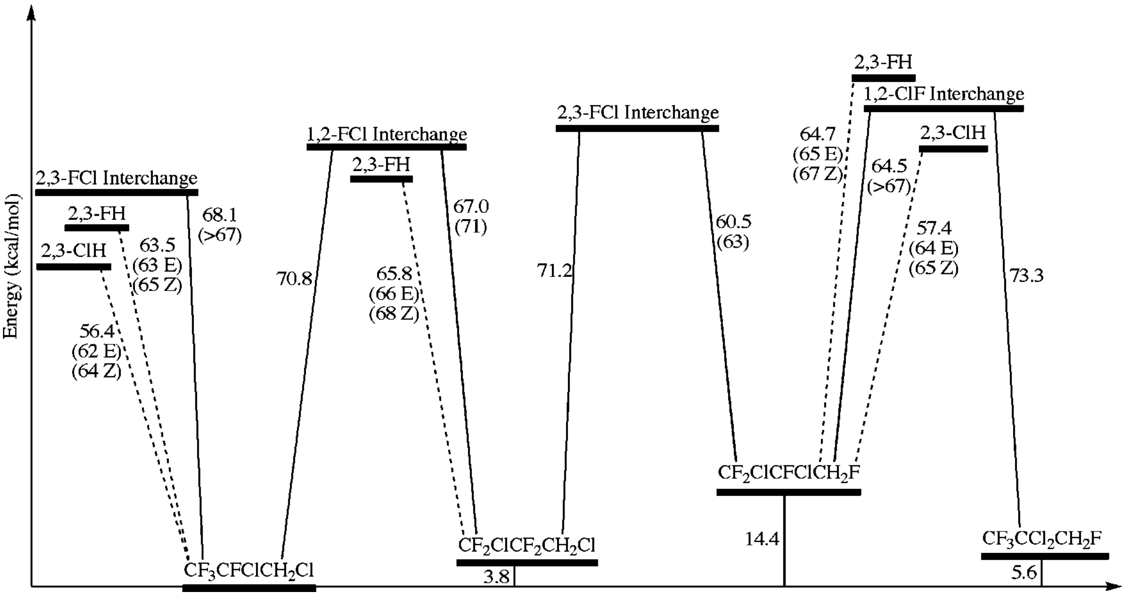

Figure 1. Diagram showing the energetic relationships between $CF_3CFClCH_2Cl$, $CF_2ClCF_2CH_2Cl$, $CF_2ClCFClCH_2F$ and $CF_3CCl_2CH_2F$ and their transition states. The reference energy is the energy of formation of $CF_3CFClCH_2Cl$. The values in parentheses are the experimentally assigned threshold energies. The other values are calculated energies from the 6-31G(d′,p′) basis set for lowest energy conformers and only the result for the *E* isomer is shown. All these structures are on the same relative scale because they are isomeric structures.

TABLE 1: Experimental Rate Constants[a] for $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$

	$CF_2ClCF_2CH_2Cl$		$CF_2ClCFClCH_2F$	
reactions	Torr (10^{-4})	s^{-1} (10^4)[b]	Torr (10^{-4})	s^{-1} (10^4)[b]
2,3-FH elimination				
trans-FH	3.16 ± 0.16	0.41 ± 0.12	0.73 ± 0.05	0.095 ± 0.028
cis-FH	0.81 ± 0.04	0.11 ± 0.03	0.18 ± 0.02[c]	0.023 ± 0.006
2,3-ClH elimination				
trans-ClH			5.32 ± 0.45	0.69 ± 0.20
cis-ClH			2.04 ± 0.15	0.27 ± 0.06
ClF-interchange				
1,2-ClF	0.13 ± 0.03	0.017 ± 0.004	observed, but rate constant too small to measure[d]	
2,3-ClF	not observed		2.06 ± 0.11	0.27 ± 0.08

[a] Rate constants for molecules formed in reactions 1 and 2. The stated uncertainty of the rate constants in Torr units is the least-squares error from the D_i/S plots. The overall uncertainty was increased to ±30% for rate constants in s^{-1} units. [b] A constant factor of 1.3×10^7 s/Torr was used to convert from Torr to s^{-1}; this factor was used in ref 1 for $CF_3CFClCH_3{}^*$ in $CH_3I + CF_3CFClI$ bath gas. [c] The rate constant for *cis*-$CF_2ClCCl{=}CHF$ formation was obtained from estimates for the trans/cis ratio; see text. [d] Products from 1,2-ClF interchange ($CF_3CCl_2CH_2F + CF_3CCl{=}CHF$) could be observed in GC/MS experiments, but the yields were too small to permit D_i/S measurements. As an estimate $k(\text{1,2-ClF}) \leq 0.1\ k(\text{2,3-ClF})$.

conformer for the molecule and the lowest energy conformer for each transition state. Several internal rotational energy barriers for $CF_2ClCF_2CH_2Cl$ were checked to ensure that barrier heights from similar molecules were transferable. Previous studies[2,3,5] have shown that the rate constants are not sensitive to modest (±30%) changes in rotational barriers, and in the present work rate constants for free rotors were done for comparison. Further, the calculated rate constants are not sensitive to modest changes in the values of two or three frequencies, unless the lowest frequencies are altered, but in this case the low frequency torsions have been replaced by internal rotors. The use of an average conformer for the molecule for computation of the rate constants will reduce the reliability of the assigned threshold energies; however, the $\langle E \rangle$ and the experimental measurement of the rate constants probably are the major sources of uncertainty. Inspection of ref 7 in which the $CF_2ClCHFC_2H_5$ system was treated provides further illustration of the application of RRKM computations to systems with a large number of conformers.

The average energy of the molecules formed by recombination of the radicals is an essential property in assigning the E_0 values of the subsequent unimolecular reactions. The $\langle E \rangle$ is obtained from the enthalpies of formation of the reactants and products, but these are not known from experimental measurements or from reliable computations for $CF_2ClCFCl$ or for $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$. Therefore, isodesmic reaction schemes and calculated isomerization energies were employed to find realistic estimates for these enthalpies of formation.

All electronic structure calculations for rate constants were done with the Gaussian suite[8] of codes using DFT with the B3PW91/6-31G(d′,p′) method. Results from this method provide satisfactory structures and usually close agreement between calculated and experimentally assigned E_0 values for HF elimination reactions.[1-7] The agreement between the calculated and experimental E_0 values for HCl elimination and for ClF interchange is frequently less pleasing, but the trends in E_0 values are still useful.

2. Experimental Methods

The experiments consist of ultraviolet photolysis of equal molar mixtures of CF_2ICF_2Cl with CH_2ICl and $CF_2ClCFClI$ with either CH_2IF or $(CH_2F)_2CO$ in large Pyrex glass or quartz vessels at room temperature. The Pyrex vessels also contained trace amounts of Hg_2I_2 to aid in radical formation. The mixtures were photolyzed at selected low pressures with either a 200 or 500 W high pressure Hg lamp and subsequently analyzed by gas chromatography for the reaction products. Except for CH_2IF, which was synthesized in our laboratory, the 1,3-difluoroacetone and the iodides were purchased from either SynQuest or Oakwood products. Because the quantity of CH_2IF was limited and the preparation was difficult to purify, most experiments requiring CH_2F radicals were done with $(CH_2F)_2CO$. The iodide and acetone molecules photodissociate and the resulting radical recombination reactions are listed in reactions 1 and 2. The asterisk denotes vibrational excitation.

$$CF_2ClCF_2 + CH_2Cl \rightarrow CF_2ClCF_2CH_2Cl^* \tag{1a}$$

$$\rightarrow CH_2ClCH_2Cl^* \tag{1b}$$

$$\rightarrow CF_2ClCF_2CF_2CF_2Cl^* \tag{1c}$$

$$CF_2ClCFCl + CH_2F \rightarrow CF_2ClCFClCH_2F^* \tag{2a}$$

$$\rightarrow CH_2FCH_2F^* \tag{2b}$$

$$\rightarrow CF_2ClCFClCFClCF_2Cl^* \tag{2c}$$

The CF_2ClCF_2 and $CF_2ClCFCl$ radicals also undergo disproportionation reactions to give $C_2F_4 + CF_2ClCF_2Cl$ (or CH_2Cl_2) and $C_2F_4 + CF_2ClCFCl_2$ (or CH_2ClF) products. The $C_2H_4Cl_2^*$ and $C_2H_4F_2^*$ molecules decompose by HCl and HF elimination at the low pressures of these experiments and C_2H_3Cl and C_2H_3F are the observed products from these recombination events. Our interest is in the unimolecular reactions of $CF_2ClCF_2CH_2Cl^*$ and $CF_2ClCFClCH_2F^*$, which are listed in (3) and (4). Reactions (3c) and (4e) represent collisional stabilization by bath gas molecules, M.

$$CF_2ClCF_2CH_2Cl^*$$

$$\rightarrow HF + CF_2ClCF{=}CHCl \text{ (cis and trans)} \tag{3a}$$

$$\rightarrow CF_3CFClCH_2Cl^* \quad \Delta H^\circ = -3.8 \text{ kcal mol}^{-1} \tag{3b}$$

$$+ M \rightarrow CF_2ClCF_2CH_2Cl + M \tag{3c}$$

The 2,3-FCl interchange reaction, which is 10.6 kcal mol^{-1} endothermic, is not competitive with 1,2-ClF interchange, hence it is not listed in (3). The $CF_3CFClCH_2Cl^*$ system[2] has been experimentally characterized, and the expected ratio of collisionally stabilized and decomposed molecules at a given pressure is known. The 1,2-ClF interchange channel is represented by the sum of the yields of $CF_3CFClCH_2Cl$ plus *cis*- and *trans*-$CF_3CF{=}CHCl$.

The $CF_2ClCFClCH_2F^*$ molecule has four possible unimolecular reaction pathways, if both 1,2-ClF and 2,3-ClF interchange processes are included. The 1,2-FCl interchange to give $CFCl_2CF_2CH_2F$ has a higher threshold energy than 1,2-ClF interchange, and the 1,2-FCl interchange reaction is not listed.

$$CF_2ClCFClCH_2F^*$$

$$\rightarrow HCl + CF_2ClCF{=}CHF \text{ (cis and trans)} \tag{4a}$$

$$\rightarrow HF + CF_2ClCCl{=}CHF \text{ (cis and trans)} \tag{4b}$$

$$\rightarrow CF_2ClCF_2CH_2Cl^* \quad \Delta H^\circ = -10.6 \text{ kcal mol}^{-1} \tag{4c}$$

$$\rightarrow CF_3CCl_2CH_2F^* \quad \Delta H^\circ = -8.8 \text{ kcal mol}^{-1} \tag{4d}$$

$$+ M \rightarrow CF_2ClCFClCH_2F + M \tag{4e}$$

The 1,2- and 2,3-ClF isomerizations are exothermic and the $CF_2ClCF_2CH_2Cl^*$ and $CF_3CCl_2CH_2F^*$ molecules will decompose by 2,3-FH and 2,3-ClH elimination, respectively, or be collisionally stabilized by bath gas, M. The HCl and HF elimination reactions of $CF_2ClCFClCH_2F^*$, $CF_2ClCF_2CH_2Cl^*$, and $CF_3CFClCH_2Cl^*$ generate chemically different fluorochloropropene products and each process in (4) can be identified. The $CF_2ClCF_2CH_2Cl^*$ system was characterized prior to attempting the $CF_2ClCFClCH_2F^*$ experiments; therefore, the gas chromatographic retention times for the products from (3) were already known, which greatly aided identification of the $CF_2ClCF_2CH_2Cl$ molecules formed in (4c). Both CH_2IF and $(CH_2F)_2CO$ were used as sources of CH_2F radicals and the same results were obtained in both experiments.

These experiments (gas handling, preparation of samples for photolysis, the photolysis lamps, gas chromatographic analysis with either flame ionization (FID) or mass spectrometric (MS) detection, etc. were done with the same facilities as previously described for the $CF_3CFClCH_2Cl$ system.[2] Therefore, a detailed description of the equipment and procedures is not necessary. Only $CF_2ClCF{=}CHF$ (and $CF_3CF{=}CHCl$[2]) could be identified by comparison with an authentic sample; other products were identified by gas chromatography with mass spectroscopic detection. A $CF_2ClCF{=}CHF$ sample was synthesized in our laboratory by the photolysis of CF_2ClI with $CHF{=}CHF$. The disproportionation reaction of $CF_2ClCHFCHF$ radical gives $CF_2ClCF{=}CHF$; the mass spectrum from this synthesis matched that from the $CF_2ClCFClCH_2F$ system, e.g., reaction 4. The yield of the trans isomer of fluorochloropropenes (or butenes)[2,7] is 3−5 times higher than the yield of the *cis* isomer, and that criteria served to distinguish between the GC peaks of the cis and trans isomers from reactions 3 and 4.

The data for the D_i/S vs pressure^{-1} plots were obtained from GC−FID measurements. A 60 m by 0.25 mm RTX-VMS capillary column was used for the $CF_2ClCFClCH_2F$ system. The temperature program was 20 min at 35° followed by heating at a rate of 6 °C /min to a final temperature of 180 °C. The approximate retention times in minutes for major products were 8.3 (*trans*-$CF_2ClCF{=}CHF$), 8.9 (*cis*-$CF_2ClCF{=}CHF$), 21.7 ($CF_2ClCFClCH_2F$), and 22.2 ($CF_2ClCF_2CH_2Cl$). The same temperature program was used with a 0.53 mm by 105 m MXT-624 column for the $CF_2ClCF_2CH_2Cl$ system. The retention times were 25.9 (*trans*-$CF_2ClCF{=}CHCl$), 27.1 (*cis*-$CF_2ClCF{=}CHCl$), and 28.9 ($CF_2ClCF_2CH_2Cl$). Because authentic samples of $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$ were not available, we used the same calibration factors to convert the GC−FID data to D_i/S ratios that were employed in the $CF_3CFClCH_2Cl$ system.[2] These factors are 1.30 for $CF_2ClCF{=}CHCl/CF_2ClCF_2CH_2Cl$, 1.53 for $CF_2ClCF{=}CHF/CF_2ClCFClCH_2F$ and 1.30 for $CF_2ClCCl{=}CHF/CF_2ClCFClCH_2F$. The response factor for $CF_2ClCF_2CH_2Cl/CF_2ClCFClCH_2F$ was assumed to be unity. The sensitivity of both the GC−MS and GC−FID response to cis and trans isomers can confidently assumed to be the same.

3. Experimental Results

3a. $CF_2ClCF_2CH_2Cl$ System. Experiments to measure the ratio of decomposition (D_i) to stabilization (S) product ratios were done over the pressure range (0.02−1.8) × 10^{-3} Torr. This range of pressure corresponds to the low pressure limit of the experimental technique, and the results do show more experimental uncertainty than similar studies at higher pressures. The D_i/S ratios are plotted vs pressure^{-1} in Figure 2. The extent of decomposition of $CF_2ClCF_2CH_2Cl$ is less than 20%, even at the lowest pressure. Linear fits to the points in Figure 2 gave rate constants of 3.16 × 10^{-4} and 0.81 × 10^{-4} Torr for the formation of *trans*-$CF_2ClCF{=}CHCl$ and *cis*-$CF_2ClCF{=}CHCl$,

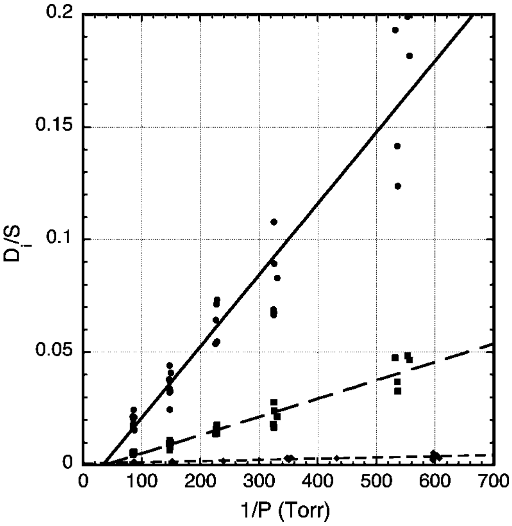

Figure 2. Plots of D_i/S vs pressure^{-1} for 2,3-FH elimination and 1,2-ClF interchange from $CF_2ClCF_2CH_2Cl$*: (●) *trans*-$CF_2ClCF{=}CHCl$/$CF_2ClCF_2CH_2Cl$; (■) *cis*-$CF_2ClCF{=}CHCl/CF_2ClCF_2CH_2Cl$; (◆) (*trans*- + *cis*-$CF_3CF{=}CHCl$ + $CF_3CFClCH_2Cl$)/$CF_2ClCF_2CH_2Cl$.

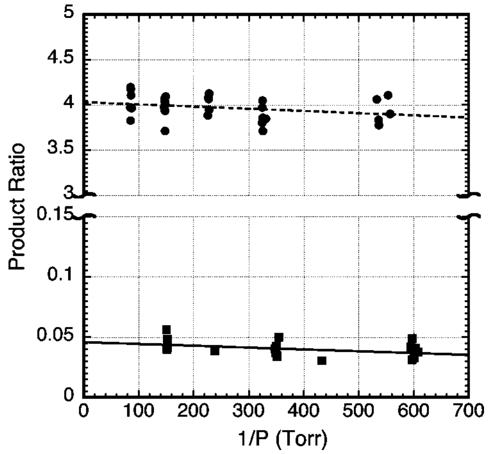

Figure 3. Plots of trans/cis ratios for 2,3-FH elimination from $CF_2ClCF_2CH_2Cl$*, ●, and the product ratio (*trans*- + *cis*-$CF_3CF{=}CHCl$ + $CF_3CFClCH_2Cl$)/*trans*-$CF_2ClCF{=}CHCl$, ■. $CF_3CFClCH_2Cl$ was formed from 1,2-ClF interchange of $CF_2ClCF_2CH_2Cl$*.

respectively. These rate constants, which were obtained by GC−FID measurements, give a trans/cis ratio of 3.9. The ratios obtained from individual experiments with measurements by GC−MS are shown in Figure 3; the average is 4.0. The two data sets agree and the overall average trans/cis ratio for $CF_2ClCF{=}CHCl$ is 4.0. Although 2,3-FH elimination is the dominant reaction, the presence of $CF_3CFClCH_2Cl$ and its main decomposition product, *trans*- and *cis*-$CF_3CF{=}CHCl$, were also observed in low yield by GC−MS measurements. The trans/cis ratio of $CF_3CF{=}CHCl$ is 3.3, which matches the ratio from our prior study[2] of $CF_3CFClCH_2Cl$*.

The D_i/S plot for 1,2-ClF interchange also is shown in Figure 2. The rate constant deduced from the D_i/S plot is 0.055×10^{-4} Torr with a large uncertainty because of the difficulty of measuring the low product yield from 1,2-ClF interchange. The plot of the 1,2-ClF interchange product to *trans*-$CF_2ClCF{=}CHCl$ in Figure 3 gives a branching of 0.04, and converting this ratio to a rate constant gives 0.13 ± 0.03 Torr for ClF interchange. Both of these rate constant are based upon uncalibrated mass spectrometric total ion-current measurements for the product ratios. We believe that the low pressure results for the ($CF_3CF{=}CHCl$ + $CF_3CFClCH_2Cl$)/*trans*-$CF_2ClCF{=}CHCl$ ratio are the most reliable, and we used these data to obtain the preferred rate constant lised in Table 1. Although the 1,2-ClF interchange reaction is a minor component of the unimolecular decomposition, its identification was certain because of the earlier characterization of the isolated $CF_3CFClCH_2Cl$ system.[2] No evidence was found for products that could be associated with 2,3-FCl interchange.

The rate constants in pressure units were converted to s^{-1} units with the same factor[1,2] previously used with $CF_3CFClCH_3$ and $CF_3CFClCH_2Cl$, and the results are summarized in Table 1. This common factor was employed because the collision cross sections are not known for halogenated iodide molecules and the assumed changes in cross sections would be balanced by the increase in reduced mass of the collision pairs. The least-squares uncertainties in the slopes of the D_i/S plots, typically 10%, were increased to ±30% for the rate constants in s^{-1} units to allow for the uncertainty in the GC calibration factors and in the conversion factor to s^{-1}. The actual uncertainty in k(1,2-ClF) could be ±50%.

3b. $CF_2ClCFClCH_2F$ System. The majority of the experiments utilized $(CH_2F)_2CO$ as the CH_2F radical source, but the results were the same with a limited number of experiments using CH_2FI. The pressure range for these experiments was from 0.2 to 0.006 Torr. The 2,3-ClH elimination gives *trans*- and *cis*-$CF_2ClCF{=}CHF$ and 2,3-FH elimination gives *trans*- and *cis*-$CF_2ClCCl{=}CHF$. In fact, only *cis*-$CF_2ClCF{=}CHF$ and *trans*-$CF_2ClCCl{=}CHF$ could be resolved from interfering products in GC−FID experiments, and only these two D_i/S plots are shown in Figure 4. These data gave rate constants for *cis*-ClH (2.04×10^{-4} Torr) and *trans*-FH (0.73×10^{-4} Torr) elimination. The trans/cis ratio was measured as 2.6 for ClH elimination from GC−MS data, which are displayed in Figure 5. The rate constant from the D_i/S plot can be scaled to obtain 5.32×10^{-4} Torr as the rate constant for *trans*-ClH elimination. The trans/cis ratio for $CF_2ClCCl{=}CHF$ was not measured; however, the ratio is expected to be similar to that for FH elimination from $CF_2ClCF_2CH_2Cl$, which was 4.0. Thus, the *cis*-$CF_2ClCCl{=}CHF$ formation rate constant was estimated as 0.18×10^{-4} Torr. These ClH and FH elimination rate constants are summarized in Table 1.

The 2,3-ClF interchange reaction to give $CF_2ClCF_2CH_2Cl$* was readily observed; the yields of $CF_2ClCF{=}CHCl$ and $CF_2ClCF_2CH_2Cl$ were combined to represent the total interchange product for the D_i/S plot shown in Figure 4. The linear fit to the points gives a rate constant of 2.06×10^{-4} Torr for 2,3-ClF interchange, and the branching ratio between interchange and ClH elimination is 0.28. The trans/cis ratio for $CF_2ClCF{=}CHCl$ from the GC−MS data was 3.8 (see Figure 5), which agrees with the measurement, Figure 3, from the independent study of $CF_2ClCF_2CH_2Cl$. This agreement confirms the assignments to products in the chromatograms. The $CF_3CCl_2CH_2F$ and $CF_3CCl{=}CHF$ products from 1,2-ClF interchange in $CF_2ClCFClCH_2F$ could be detected, but the yield was too low to establish a rate constant. As an estimate, k(1,2-ClF) is about 0.1k(2,3-ClF).

The experimental rate constants in Torr and s^{-1} units are summarized in Table 1. The rate constants for 2,3-FH elimination from $CF_2ClCF_2CH_2Cl$ and $CF_3CFClCH_2Cl$ (see Table 2) are similar, but k(FH) for $CF_2ClCFClCH_2F$ is 4 times smaller. The rate constant for 2,3-ClH elimination from $CF_2ClCFClCH_2F$ is 3 times smaller that for $CF_3CFClCH_2Cl$.

An added bonus from the 2,3-ClF interchange process is the opportunity to measure the rate constants for FH elimination from $CF_2ClCF_2CH_2Cl$* with approximately 6 kcal mol^{-1} more

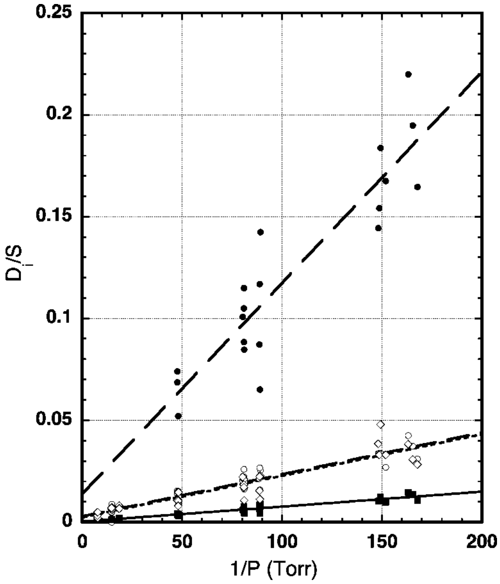

Figure 4. Plots of D_i/S vs pressure^{-1} for the $CF_2ClCFClCH_2F^*$ system: (●) *trans*-$CF_2ClCF{=}CHCl/CF_2ClCF_2CH_2Cl$ (FH loss from $CF_2ClCF_2CH_2Cl^*$ formed from 2,3-ClF interchange from $CF_2ClCFClCH_2F^*$); (◇) *cis*-$CF_2ClCF{=}CHF/CF_2ClCFClCH_2F$ (ClH loss from $CF_2ClCFClCH_2F^*$); (○) (*trans* + *cis*-$CF_2ClCF{=}CHCl + CF_2ClCF_2CH_2Cl$)/$CF_2ClCFClCH_2F$ (2,3-ClF interchange from $CF_2ClCFClCH_2F^*$); (■) *trans*-$CF_2ClCCl{=}CHF/CF_2ClCFClCH_2F$ (FH loss from $CF_2ClCFClCH_2F^*$). Note that the *trans*-$CF_2ClCF{=}CHF$ and *cis*-$CF_2ClCCl{=}CHF$ from ClH and FH loss, respectively, were not recorded for $CF_2ClCFClCH_2F^*$.

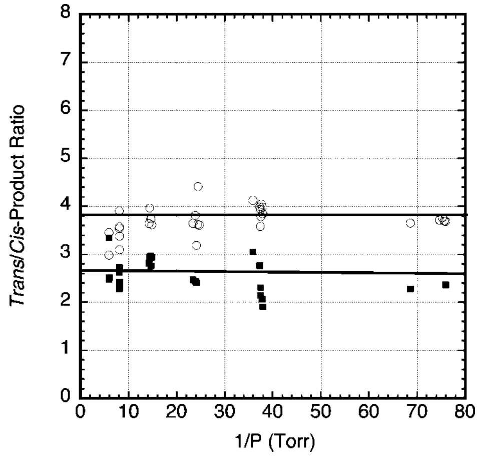

Figure 5. Plots of trans/cis ratios vs pressure^{-1} of $CF_2ClCF{=}CHF$ from 2,3-ClH loss from $CF_2ClCFClCH_2F^*$, ■, and of $CF_2ClCF{=}CHCl$, ○, from 2,3-FH loss from $CF_2ClCF_2CH_2Cl^*$ formed by 2,3-ClF interchange. Note that this trans/cis ratio from $CF_2ClCF_2CH_2Cl$ agrees with the ratio in Figure 3.

energy that the molecules formed by recombination in reaction 3. This D_i/S vs pressure^{-1} plot for *trans*-$CF_2ClCF{=}CHCl$ is shown in Figure 4. Comparison of Figure 4 with Figure 2 shows that the slope is 3−4 times higher in Figure 4. The actual rate constant from the D/S plot is $(13 \pm 3) \times 10^{-4}$ Torr, which is 3.3 ± 1.2 times larger than for $CF_2ClCF_2CH_2Cl^*$ formed by radical combination.

4. Computational Results

4a. Computational Models. The calculation of energies and structures of molecules and transition states were done with the Gaussian suite of codes. Most calculations were done with the B3PW91/6-31G(d′,p′) method. As mentioned in the Introduction, the $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$ systems have many conformers, and we have based the rate constant calculations on the structure of the average conformer for the molecule and the lowest energy conformer for each transition state. All torsional modes were treated as hindered internal rotors for the CH_2Cl (or CH_2F) and CF_2Cl groups. The barrier for the CF_2Cl group (4.3 kcal mol^{-1}) was taken from the study of $CF_2ClCF_2CH_3$[3a] and the barrier for the CH_2Cl(or CH_2F) group, 3.9 (or 3.6 kcal mol^{-1}), was selected by analogy to $CF_3CFClCH_2Cl$.[2] The most stable conformer for $CF_2ClCF_2CH_2Cl$ has the Cl atom of the CH_2Cl group trans to the CF_2Cl group of CF_2ClCF_2 and the Cl atom of the CF_2Cl group trans to the CH_2Cl group of CF_2CH_2Cl. The maximum energy difference between the most and least stable conformers is 2.7 kcal mol^{-1}. The most stable conformer of $CF_2ClCFClCH_2F$ has the F atom of the CH_2F group trans to the F atom of $CFClCF_2Cl$ and the Cl atom of the CF_2Cl group trans to CH_2F of $CFClCH_2F$. However, rotation of the CH_2F group to its other two positions only increases the energy by 0.13 and 0.33 kcal mol^{-1}. The difference between the most and least stable conformers of $CF_2ClCFClCH_2F$ is only 1.3 kcal mol^{-1}. $I_{red}(CH_2Cl)$ and $I_{red}(CH_2F)$ are 41.4 and 21.8 amu Å^2, and $I_{red}(CF_2Cl)$ is 83.7 and 83.2 amu Å^2 for $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$, respectively. The transition states have only one internal rotation and I_{red} was calculated

TABLE 2: Summary of the Experimental and Calculated Rate Constants and Threshold Energies[a] for $CF_2ClCF_2CH_2Cl$, $CF_2ClCFClCH_2F$, $CF_3CFClCH_2Cl$, $CF_2ClCF_2CH_3$ and $CF_3CFClCH_3$

	rate constants (10^4) s^{-1}			
molecule	experimental	calculated	⟨E⟩, kcal mol^{-1}	E_0, kcal mol^{-1}
$CF_2ClCF_2CH_2Cl$[b]			91 (89)	
trans-FH	0.41 ± 0.12	0.58 (0.54)		66 (65)
cis-FH	0.11 ± 0.03	0.16 (0.14)		68 (67)
1,2-ClF	0.017 ± 0.004	0.019 (0.015)		71 (70)
2,3-ClF	not observed			
$CF_2ClCFClCH_2F$[b]			87	
trans-ClH	0.69 ± 0.17	0.67		64
cis-ClH	0.27 ± 0.06	0.31		65
2,3-ClF	0.27 ± 0.08	0.29		63
1,2-ClF[d]	≤0.03			≥67
trans-FH	0.095 ± 0.028	0.12		65
cis-FH	0.023 ± 0.01	0.033		67
$CF_3CFClCH_2Cl$[c]			87	
trans-ClH	1.9 ± 0.6	1.8		62
cis-ClH	0.57 ± 0.17	0.53		64
trans-FH	0.33 ± 0.10	0.38		63
cis-FH	0.054 ± 0.016	0.062		66
2,3-FCl[d]	≤0.03	0.023		≥67[d]
$CF_2ClCF_2CH_3$[e,f]			96	
FH	65 ± 10	70		64.0
1,2-ClF	4.3 ± 0.6	4.7		66.0
$CF_3CFClCH_3$[f,g]			94	
ClH	474 ± 28	480		58.5
FH	56 ± 3	52		61.3

[a] The presence of several conformers for the molecule and the transition states should be remembered. Therefore, each assigned E_0 value is a global average. [b] This work. The calculated rate constants and E_0 values in parentheses for $CF_2ClCF_2CH_2Cl$ are for ⟨E⟩ = 89 kcal mol^{-1} to illustrate the effect of changing ⟨E⟩ on the assignment of E_0. [c] Reference 2. [d] The E_0(1,2-ClF) from $CF_2ClCFClCH_2F$ and E_0(2,3-FCl) from $CF_3CFClCH_2Cl$ are lower limits because they are based upon estimates for the experimental rate constants. [e] References 3 and 4. [f] Because the experimental data were more reliable for $CF_3CFClCH_3$ and $CF_2ClCF_2CH_3$, the E_0 assignments were adjusted to tenths of a kcal mol^{-1} to obtain closer agreement with the experimental rate constants. For the $C_3F_4H_2Cl_2$ isomers, the data only merit two significant figures for E_0. [g] Reference 1.

for each case, but the differences are small relative to the molecule. The actual values are given in the supplementary tables together with the vibrational frequencies and overall moments of inertia for the molecules and their transition states.

RRKM rate constants were calculated for various values of E_0 according to the usual formula given in equation 5. The sums of states for the transition state, $\Sigma P^\dagger(E - E_0)$, and the density of states, N_E^*, were calculated by the Multi-Well code of Barker[9] with hindered internal rotor representation for the torsional modes. The $(I^\dagger/I)$ is the ratio of the three overall moments of inertia for the transition state and the molecule.

$$k_E = s^\dagger/h(I^\dagger/I)^{1/2}\Sigma P^\dagger(E - E_0)/N_E^* \qquad (5)$$

Because $CF_3CFClCH_3$, $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$ are isomers with very similar transition states for 2,3-ClH and 2,3-FH elimination, the N_E^* and $\Sigma P^\dagger(E - E_0)$ values are all quite similar for common values E and E_0. Thus, differences in rate constants must mainly arise from different values for $\langle E\rangle$ and E_0.

4b. Thermochemistry. The average energy of the newly formed molecules is given by $D_0(R_1 - R_2)$ plus the average thermal energies of R_1 and R_2. Thus, the enthalpies of formation of R_1, R_2 and R_1–R_2 are required. The enthalpies of formation for CH_2F, CH_2Cl and CF_2ClCF_2 are −7.5,[10] +28.0,[11] and −166[3c] kcal mol^{-1} at 298 K. We obtained an estimate for $CF_2ClCFCl$ by considering the enthalpy changes for the following two reaction

$$CF_3CF_2H + CH_2ClCH_2Cl \rightarrow CF_2ClCFClH + CH_2FCH_2F \qquad (6)$$

$$CF_2ClCFClH \rightarrow CF_2ClCFCl + H \qquad (7)$$

Calculations with the 6-31G(d′,p′) and 6-311+G(2d,p) basis sets were done to obtain an average ΔH^o_0 of 23.2 kcal mol^{-1} for (6), which gave $\Delta H^o_{f,298}(CF_2ClCFClH)$ of −169.4 kcal mol^{-1} when combined with the known ΔH^o_f values of the other components.[12,13] The D_{298}(H−CFClCF$_2$Cl) value[14] of 97.0 kcal mol^{-1} was then used to find $\Delta H^o_{f,298}(CF_2ClCFCl) = -124.4$ kcal mol^{-1}. This value leads to D(F−CFClCF$_2$Cl)[15] = 109.6 kcal mol^{-1}, which is reasonable relative to other C−F bond dissociation energies.

The $\Delta H^o_f(CF_2ClCF_2CH_2Cl)$ and $\Delta H^o_f(CF_2ClCFClCH_2F)$ have not been reported. However, 5 different isodesmic reactions were used in ref 2 to establish an average $\Delta H^o_{f,298}(CF_3CFClCH_2Cl) = -230$ kcal mol^{-1}. This value can be combined with the isomerization energies, which also were calculated in ref 2 and are shown in Figure 1, to obtain $\Delta H^o_{f,298} = -226$ and −216 kcal mol^{-1} for $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$, respectively. In the present work we added one more isodesmic reaction and calculated ΔH^o_0 for reaction 8.

$$CF_2ClCF_2CH_3 + C_2H_5Cl \rightarrow CF_2ClCF_2CH_2Cl + C_2H_6 \qquad (8)$$

The values were 7.1 and 7.7 kcal mol^{-1} for the 6-31G(d′,p′) and 6-311+G(2d,p) basis sets, respectively. Combining the average, $\Delta H^o_0 = 7.4$ kcal mol^{-1}, with the accepted enthalpies of formation of C_2H_6 and C_2H_5Cl plus that of $CF_2ClCF_2CH_3 = -225$ kcal mol^{-1} from isodesmic calculations[3] gave $\Delta H^o_{f,298}(CF_2ClCF_2CH_2Cl) = -224.4$ kcal mol^{-1}, which is in excellent agreement with the value based on the average ΔH^o_0 from the 5 other isodesmic reactions and the calculated isomerization energies.

Combining the relevant enthalpies of formation gives the enthalpy changes for the recombination reactions at 298 K of −88 and −84 kcal mol^{-1} for reactions 3 and 4, respectively. Converting to 0 K and adding the thermal energies of the radicals gives $\langle E\rangle = 91$ and 87 kcal mol^{-1} for $CF_2ClCF_2CH_2Cl^*$ and $CF_2ClCFClCH_2F^*$, respectively. The uncertainty in these values is 2−4 kcal mol^{-1}.

4c. Assignment of Threshold Energies. The threshold energies were assigned by matching k_{expt} to $k_{\langle E\rangle}$, treating E_0 as a variable in eq 5. The calculated values of the rate constants and E_0 values are summarized in Table 2 for all three $C_3F_4H_2Cl_2$ isomers. Two calculated rate constants and two E_0 values are listed for each channel of $CF_2ClCF_2CH_2Cl$ corresponding to $\langle E\rangle = 91$ and 89 kcal mol^{-1} to illustrate the effect of the average energy on the assignment of E_0. A 2 kcal mol^{-1} change in $\langle E\rangle$ is equivalent to a 1 kcal mol^{-1} change in E_0, and a 2 kcal mol^{-1} reduction in E_0 increases the rate constant by a factor of 3.5 at $E = 90$ kcal mol^{-1}. Figure 3 of ref 2 can be consulted for more information about the dependence of E_0 and k_E upon $\langle E\rangle$. The existence of several conformers for the molecule plus three conformers for each transition state associated with internal rotation of the CF_2Cl, CH_2Cl and CH_2F groups must be remembered. Thus, these assigned E_0 values are global averages.

The 4-fold difference in rate constants for *trans*- and *cis*-$CF_2ClCF{=}CHF$ formation from $CF_2ClCF_2CH_2Cl$ correspond to a 2 kcal mol^{-1} higher E_0(2,3-FH) for the *cis* channel, and this conclusion is independent of any uncertainty in $\langle E\rangle$. The E_0 for *trans*-FH elimination is 65−66 kcal mol^{-1}, which is 2−3 kcal mol^{-1} higher than for $CF_3CFClCH_2Cl$. The exact difference depends on the $\langle E\rangle$ values, but the trend can be accepted. Although the transition state for ClF interchange has a slightly smaller $\Sigma P^\dagger(E - E_0)^*$ than for FH elimination for the same $E - E_0$, the threshold energy for the 1,2-ClF channel must be ≥70 kcal mol^{-1}, because the interchange rate constant is 6 times smaller than for *cis*-FH elimination.

The rate constant for *trans*-2,3-ClH elimination is 2 times larger than that for 2,3-FCl interchange in $CF_2ClCFClCH_2F$; however, the $\Sigma P^\dagger(E - E_0)$ is larger for the ClH transition state than for the interchange transition state and the E_0(interchange) must be 1−2 kcal mol^{-1} lower than E_0(*trans*-ClH). The differences in threshold energies between the trans- and cis-channels for ClH and FH elimination are about 2 kcal mol^{-1} just as for $CF_2ClCF_2CH_2Cl$. If $\langle E\rangle = 87$ kcal mol^{-1} is accepted for $CF_2ClCFClCH_2F$, then the E_0 values for *trans*-FH elimination, *trans*-ClH elimination and 2,3-FCl interchange are 65, 64 and 63 kcal mol^{-1}, respectively. The yields of the 1,2-FCl interchange products were too small to permit assignment of a rate constant, but based on the estimate for the lower limit rate constant, the E_0(1,2-FCl) must be ≥67 kcal mol^{-1}. These results are summarized in Table 2, and the assigned and the DFT calculated E_0 values are compared in Figure 1.

5. Discussion

Our original interest in these three isomeric systems was to demonstrate ClF interchange for a molecule that did not involve a CF_2Cl group. Indeed, 2,3-ClF interchange from the CH_2F group of $CF_2ClCFClCH_2F$ does provide such an example. In fact, E_0(2,3-ClF) is slightly smaller than E_0(2,3-ClH), and ClF interchange is the reaction pathway with the lowest threshold energy. The difference in enthalpies of reaction between 1,2-ClF and 2,3-ClF interchange for $CF_2ClCFClCH_2F$ is only 1.8 kcal mol^{-1}, and the preference for the 2,3-ClF pathway is a consequence of the lower threshold energy of the 2,3-ClF(isomer) transition state (see Figure 1). This difference in threshold energies, which according to the calculations is 4.1 kcal mol^{-1}, is a consequence of the presence of two H atoms for the 2,3-Cl-F transition state vs two F atoms for the 1,2-ClF transition state that are attached to the bridged carbon atoms. The C−H bond energy increases for a sp^2 C atom vs a sp^3 C atom, whereas the C−F bond dissociation energy remains roughly constant, and because the C atoms in the exchange transition state have a nearly sp^2 structure, the presence of H atoms lowers the E_0 for ClF interchange. The same trend for E_0(ClF) has been found in systematic calculations[16] and experiments[17,18] for $C_2H_{6-x-y}F_xCl_y$ molecules. Although the same argument exists for 1,2- vs 3,2-ClF interchange in $CF_2ClCF_2CH_2Cl$, the 14.4 kcal mol^{-1} difference in enthalpy overcomes the C−H vs C−F bond energy effect of the transition states and 1,2-ClF interchange is favored. According to the calculations, the difference in threshold energies is just 5 kcal mol^{-1}, which is much smaller than the enthalpy difference for the two reaction channels.

The 1,2-ClF interchange process is 2−3 times more important for $CF_2ClCF_2CH_3$ (branching fraction of 0.06) than for $CF_2ClCF_2CH_2Cl$. The experimentally based E_0(1,2-ClF) for $CF_2ClCF_2CH_2Cl$ is 3−4 kcal mol^{-1} larger than for $CF_2ClCF_2CH_3$, and the DFT calculated value increased by 67.0−64.2 = 2.8 kcal mol^{-1}. The similar increase of E_0(2,3-ClH or -FH) for the $C_3F_4H_2Cl_2$ series, relative to $CF_3CFClCH_3$, can be rationalized[2] by the additional repulsion energy between the F (or Cl) and Cl atoms attached to the ring of the transition state. But, for 1,2-ClF interchange the only difference in the structures of the transition states for $CF_2ClCF_2CH_3$ vs $CF_2ClCF_2CH_2Cl$ is the CH_3 vs CH_2Cl group attached to a bridged carbon atom. On the basis of the elevated energies of the other two conformers (1.01 and 2.48 kcal mol^{-1}) of the transition state, we suspect that the increase in E_0 arises from the repulsion introduced by substitution of a Cl atom in the CH_3 group.

Although threshold energy values were assigned to the observed reaction channels of the three isomers, see Table 2, the uncertainty associated with the average energy of each isomer and the presence of several conformers reduces the reliability of the specific E_0 values. Therefore, discussion should be focused on the main trends rather that on the individual E_0 values. Before examining these trends, we can cite an experimental result that supports the thermochemistry. The 3−4-fold larger k(2,3-FH) for $CF_2ClCF_2CH_2Cl^*$ formed from reaction 4c relative to reaction 1a provides some support for the assigned $\langle E \rangle$ values. The 6.6 kcal mol^{-1} higher energy for (4c) would increase k(2,3-FH) by a factor of 8, according to the calculated rate constants. Thus, the difference in $\langle E \rangle$ values should not be any larger than the present assignment; i.e., for an isomerization energy of 10.6 kcal mol^{-1} $D(CH_2Cl{-}CF_2CF_2Cl)$ should be larger than $D(CH_2F{-}CFClCF_2Cl)$.

The most obvious general trend is the small total unimolecular rate constants of the $C_2F_4H_2Cl_2$ isomers relative to those for $CF_3CF_2CH_3$, $CF_3CFClCH_3$ or $CF_2ClCF_2CH_3$; see Table 2. As previously discussed,[2] a major factor in explaining the small rate constant for $CF_3CFClCH_2Cl$, relative to $CF_3CFClCH_3$ or $CF_3CF_2CH_3$,[19] was the reduced $\langle E \rangle$. Although the thermochemistry is somewhat uncertain, the $\langle E \rangle$ values for $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$ also are low, and the recombination of CH_2Cl or CH_2F radicals with CF_3CFCl, CF_2ClCF_2 or $CF_2ClCFCl$ radicals seems to be a few kcal mol^{-1} less exothermic than with CH_3 radicals. A second factor that contributed to the small rate constants of $CF_3CFClCH_2Cl$ was the increase in N_E^* with the change of the CH_3 group to a CH_2Cl group. The same argument holds for $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$. An additional increase in N_E^* occurs from loss of symmetry when the CF_3 group is switched to a CF_2Cl group; however, a mitigating effect exists in $\Sigma P^\dagger(E - E_0)$ for 2,3-type processes, and the net effect on the rate constants is rather insignificant. For example, the HF-elimination rate constants for all three isomers are similar at the same E and E_0 for $s^\dagger = 1.0$. An important third factor is the higher threshold energies for the $C_3F_4H_2Cl_2$ molecules (see Table 2) relative to the halopropanes with a CH_3 group rather than a CH_2F or CH_2Cl group. However, threshold energies for similar processes are not identical for the three isomers, and some of these obvious differences are examined next.

Even though the 2,3-FH rate constants for $CF_3CFClCH_2Cl$ and $CF_2ClCF_2CH_2Cl$ are nearly equal, the reaction path degeneracy is 2-fold higher and $\langle E \rangle$ is 3.0 kcal mol^{-1} larger for $CF_2ClCF_2CH_2Cl$, thus a slightly higher E_0 is required to match the experimental rate constant for $CF_2ClCF_2CH_2Cl$. The main reason that E_0(FH) is higher for $CF_2ClCF_2CH_2Cl$ is related to the difference in C−X (X = Cl, F) bond strengths for carbons that are sp^3 (reactant molecules) versus sp^2 hybridized (transition states). For example, using the calculated numbers in Figure 1, $CF_3CFClCH_2Cl$ is 3.8 kcal mol^{-1} lower in energy than $CF_2ClCF_2CH_2Cl$, but the isomeric transition states differ by 6.1 kcal mol^{-1}. We ascribe the larger energy difference for the transition states to the difference in C−Cl and C−F bond energies in the transition state for sp^2 vs sp^3 hybridized carbons in the reactant; e.g., the relative increase in strength is higher for the C−Cl bond than the C−F bond in the transition state.[6a]

Although the F and Cl atoms have exchanged positions on the ring carbon atoms in $CF_2ClCFClCH_2F$ vs $CF_2ClCF_2CH_2Cl$, the E_0(*trans*-FH) are very similar. The DFT calculated E_0(*trans*-2,3-FH) for the three molecules are 63.5, 65.8 and 64.7 kcal mol^{-1} for $CF_3CFClCH_2Cl$, $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$, respectively. As illustrated in Figure 1, the large difference in enthalpies of formation of $CF_2ClCFClCH_2F$ and $CF_2ClCF_2CH_2Cl$ also exists for their FH-elimination transition states, and thus the calculated E_0 values actually differ by only 1−2 kcal mol^{-1}. Structures with a primary F atom and a secondary Cl atom are about 10 kcal mol^{-1} less stable than structures with the converse arrangement. Switching the secondary F atom to carbon number 1 to generate CF_3 gains an additional 4 kcal mol^{-1} of energy for both the $CF_3CFClCH_2Cl$ molecule and its transition states. In summary, the trends that exist for the enthalpies of formation of the molecules also exist for the transition states and the DFT calculated E_0(FH) values are in relatively good agreement with the experimentally assigned values.

The 2,3-ClH rate constant is 3 times smaller for $CF_2ClCFClCH_2F$ than for $CF_3CFClCH_2Cl$; the $\langle E \rangle$ are similar; therefore, a 2 kcal mol^{-1} higher E_0(ClH) is required for $CF_2ClCFClCH_2F$. As shown in Figure 1, the calculated enthalpies of formation of the 2,3-ClH transition states and the $CF_3CFClCH_2Cl$ and $CF_2ClCFClCH_2Cl$ molecules follow the same pattern; i.e., the 14.4 kcal mol^{-1} isomerization energy is nearly the same for the molecules and the HCl elimination transition states. Although the threshold energy is slightly higher for the transition state of $CF_2ClCFClCH_2F$ (with CF_2Cl, F and F, H attached to the carbons) than for the transition state of $CF_3CFClCH_2Cl$ (with CF_3, F and Cl, H attached to the carbons), the additional F atom on the ring carbon atoms may not be the only factor behind the 1 kcal mol^{-1} difference in the energy of the transition states. Although the trends match the experimental results, the calculated absolute E_0(2,3-ClH) values are 6−7 kcal mol^{-1} too low. The B3PW91/6-31G(d′,p′) computational method does not provide reliable threshold energies for 2,3-ClH elimination reactions from either $CF_3CFClCH_2Cl$ or $CF_2ClCFClCH_2F$ but shows much better agreement for 2,3-FH elimination reactions.

6. Conclusions

The unimolecular reactions of chemically activated $CF_2ClCF_2CH_2Cl$ and $CF_2ClCFClCH_2F$ molecules have been characterized and compared to those of $CF_3CFClCH_2Cl^2$. The 2,3-ClF interchange reaction of $CF_2ClCFClCH_2F$ is competitive with 2,3-ClH and 2,3-FH elimination reactions. However, 1,2-ClF interchange is only a minor reaction for $CF_2ClCF_2CH_2Cl$ (and for $CF_2ClCFClCH_2F$), and neither 1,2-FCl nor 2,3-FCl interchange occurs for $CF_3CFClCH_2Cl$. The average energies of the three isomeric molecules were assigned via isodesmic calculations. The experimental rate constants were compared to RRKM calculated rate constants to assign a threshold energy to each observed reaction. The models for the calculated rate constants were based upon DFT electronic structure calculations (B3PW91/6-31G(d′,p′)). The torsional modes were treated as hindered internal rotations and the calculated rate constants represent an average conformer. The threshold energy for 2,3-ClF interchange in $CF_2ClCFClCH_2Cl$ is the lowest energy pathway, but only by 1−2 kcal mol^{-1}, for that molecule. The presence of H atoms on the bridged carbon atoms of the transition state lowers the E_0 values for ClF interchange, whereas the presence of F atoms raises the threshold energy. The same trend in E_0 exists for F and H atoms located on the carbon atoms of the four-membered ring of the transition state for FH and ClH elimination. If the interchange reaction is exothermic, the interchange process is likely to be a competitive reaction in fluorochlorocarbon alkane molecues with F and Cl atoms on adjacent carbon atoms. The smaller total unimolecular rate constants for the three $C_3F_4H_2Cl_2$ molecules, relative to analogous chemically activated molecules with a CH_3 group rather than a CH_2F or CH_2Cl group, is a consequence of a lower average energy (because of a lower $CF_2{-}CH_2X$ or CFCl-CH_2X bond dissociation energy) and somewhat higher threshold energies for HCl or HF elimination plus the expected higher density of states associated with substitution of a F or Cl atom for an H atom in the CH_3 group.

The recombination reactions of radicals or an atom plus a radical at room temperature have provided numerous chemical systems of vibrationally excited molecules that have permitted systematic studies of unimolecular reactions including both measurement of rate constants[5] and energy disposal.[20,21] The present work employed photolysis of iodide precursor molecules to generate CH_2Cl, CF_2CH_2Cl and $CFClCH_2F$ radicals for the purpose of generating halopropane molecules that permitted the observation of halogen atom exchange reactions on adjacent carbon atoms. It would be useful to explore whether DFT calculations predict that interchange reactions are relatively generic and can occur with a halogen atom and pseudo halogens groups such as OH, SH, OCH_3, CH_3 or NH_2. The future challenge is to design suitable experimental systems with vibrationally excited molecules that will permit characterization of these interchange reactions in competition with other unimolecular reaction channels.

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Supporting Information Available: Table S1 lists the calculated vibrational frequencies and moments of inertia for each conformer of $CF_2ClCF_2CH_2Cl$ and S3 has the same information for $CF_2ClCFClCH_2F$. Each table has the geometric mean used in the rate constant calculations. The computed structure for each conformer is shown. Table S2 shows the calculated vibrational frequencies and moments of inertia for 1,2-ClF interchange and for each 2,3-FH and 2,3-ClH elimination transition state of lowest energy for $CF_2ClCF_2CH_2Cl$. The computed structures for all transition states are also shown. Table S4 shows the calculated vibrational frequencies and moments of inertia for 2,3-ClF and 1,2-ClF interchange and for each 2,3-FH and 2,3-ClH elimination transition state of lowest energy for $CF_2ClCFClCH_2F$. The computed structure for each transition state is shown. All calculations used the DFT method B3PW91 level of theory with a 6-31G(d′,p′) basis set. This information is available free of charge via the Internet at http://pubs.acs.org.

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