Experimental and Computational Investigation of CH₃CHFCH₂Cl and CF₃CHFCH₂Cl: An Examination of the Effect of an Electron-donating and an Electron-Withdrawing Group on the F-Cl Interchange Unimolecular Reaction

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Abstract

The recombination reactions of CH₂Cl radicals with CF₃CHF and with CH₃CHF radicals were used to generate CF₃CHFCH₂Cl and CH₃CHFCH₂Cl molecules with 90-92 kcal mol⁻¹ of vibrational energy. The experimental rate constants for elimination of HCl and HF and the interchange of Cl and F atoms were measured and compared to RRKM calculated rate constants to assign the threshold energy for each unimolecular reaction channel. The Cl/F interchange reaction is approximately 18% of the total unimolecular reaction for both molecules. The product branching ratios and some rate constants also could be measured for the unimolecular reactions of the rearranged molecules, CF₃CHClCH₂F and CH₃CHClCH₂F. The most important result is that the CH₃ group lowers the threshold for Cl/F interchange relative to CH₂FCD₂Cl, as expected for an electron-density donating group, and the CF₃ groups alter the threshold energies of the HCl and HF elimination reactions in such a way so as to maintain the same branching fraction for the interchange reaction. The results from density functional theory using the B3PW91 method with the 6311+G(2d,p) and G-31G(d',p') basis sets are used to discuss the trends in threshold energies for the Cl/F interchange mechanism in the CH₂FCH₂Cl analog, and contributes to understanding of the reactions of the F/Cl interchange mechanism in the CH₂FCH₂Cl analog, and contributes to understanding of the reactions of the F/Cl interchange mechanism in the CH₂FCH₂Cl analog, and contributes to understanding of the reactions of the F/Cl interchange mechanism in the CH₂FCH₂Cl analog, and contributes to understanding of the reactions of hydrofluorochlorocarbons (HCFCs), which have a significant impact on global climate changes.

Keywords: CH₃CHFCH₂Cl, CF₃CHFCH₂Cl, Unimolecular Reaction

1. Background

Prediction of global warming caused by greenhouse gases dates back as early as Arrehnius' discussion of the effect of CO_2 at the end of the nineteenth century¹. Yet over 100 years later, details of the reaction mechanisms of many HCFCs are still not understood. A recent study by V. Vaida considered the physical chemistry of molecular reactions in the atmosphere, and concluded "Atmospheric aerosols play an important role in global climate and air quality, yet outstanding fundamental chemical questions preclude their accurate treatment in atmospheric models"². Aerosols and sulfate aerosols form at low altitudes and scatter incoming solar radiation, and are also significant in the atmosphere based on the contribution as a heterogeneous surface that can be a catalytic site³. Investigation of the unimolecular rates and reaction mechanisms of HCFCs aids the contemporary effort to answer these fundamental questions in the realm of atmospheric chemistry and climate change.

Both chlorofluorocarbon (CFC) and HCFC emission have caused ozone depletion⁴. CFCs have troposphere lifetimes in the realm of 540-1800 years, with removal possible only by adsorption on siliceous materials. Their

long lifetime is a result of their inability to absorb wavelengths over 290nm, or react with O₃, OH, or NO₃ at significant rates, and their low solubility in water⁵. The presence of halogenated aliphatic hydrocarbons increased in the environment due to elevated use of aerosol propellants and refrigerants⁶. The amendments and adjustments in the Montreal Protocol have led to decline in the concentration of Cl from anthropogenic sources in the troposphere, and it is possible that the same is true for the stratosphere. A special report describes greenhouse gases as those that "...absorb and emit thermal infrared radiation"⁷, and noted that halocarbons comprised 13% of the total well-mixed greenhouse gas radiative forcing that occurred from 1750-2000 (years). Halocarbons are up to thousands of times more potent absorbers of radiative energy emitted from Earth than carbon dioxide, and will continue to affect the radiative balance in the future. Stratospheric ozone protects life at earth's surface through absorption of potentially damaging UV radiation. Ozone destruction has a positive correlation with temperature increase and the concentration of radical species. The heterogeneous and multiphase chemistry carried out on condensed matter in the lower stratosphere impacts radical distribution, and ultimately causes the ozone hole in the polar lower stratosphere. The introduction of radicals from anthropologenic ozone depleting substances (ODSs) impacts the gains and losses of the stratospheric ozone distribution⁸. Forcings caused by ODSs have been decreased as a result of the Montreal Protocol, but will continue to have significant influence, which will be determined by the extent of the emission of the ODSs and their substitutes.

The Heard and Holmes research group has been studying the reaction mechanisms and rates of hydrochlorofluorocarbons for many years. In 2002 Heard and Holmes discovered an interchange mechanism that may affect the behavior of HCFC compounds⁹, and since then a series of experiments undertaken by this research group has examined unimolecular rate constants of molecules whereby Fluorine and Chlorine atoms are systematically substituted on adjacent carbons within ethanes, propanes, and butanes. The F and Cl atom exchange positions on adjacent carbons with a sp² planar structure via a bridged transition state^{10,11,12,13}.

The rate constants and threshold energies for the unimolecular reactions of such previously studied systems as $CF_2CICHFC_2H_5/C_2D_5$, $CF_2CICHFCH_3$, CF_3CHFCF_3 , and CH_3CHFCH_3 are relevant to an understanding of CF_3CHFCH_2CI . The CF_3CHFCH_2CI system is similar to $CF_2CICHFC_2H_5/C_2D_5$ system in that 1,2-FH elimination is completely negligible¹⁰. The molecules in this study were activated with 93-94 kcal/molecule of vibrational energy, comparable to the 90 kcal/mole of energy used in the study of CF_3CHFCH_2CI . The study lead by Beaver suggested that the departing Chlorine experienced a greater gain in electron density as compared to a departing Flourine, and that HCl loss resulted in a much larger increase in dipole movement as compared to HF loss¹⁰. The Cl-F interchange was identified as a rigid structure, and was a third documented example of the interchange. Addition of a C_2H_5 lowered the rate constant by a factor of 15-150 as compared to CH_3 , but the branching ratio was essentially unaffected by the substitution^{10,11}.

For CF₂ClCF₂CH₃ and CF₂ClCF₂CD₃ a small isotope effect suggested that the rate-limiting step was not indicative of C-H/C-D bond rupture^{12,13}. Electronic structure calculations proposed a rate-limiting 1,2-ClF interchange followed by fast 2,3-ClH elimination reaction^{12,13}. This study independently characterized the ClH and FH elimination reactions and the rapid rate of the HCl elimination reaction was confirmed^{12,13}. From CF₂ClCHFCH₃/CD₃, threshold energies were determined to be 57.5, 59.5, and 62.5 to ClF, HF, and HCl channels, respectively, with 1.5 kcal/mol uncertainty¹³. Along with some of the previous studies, these results confirmed the Cl-F interchange as an elementary reaction that can compete with HCl and HF elimination for halogenated alkanes with Cl and F on neighboring carbons¹². The interchange process is observed in fully halogenated fluorochloroethanes and propanes, even though the threshold energy is high relative to other decomposition pathways¹³. The transition state was concluded from DFT computational calculations to be a double-bridged structure with the F and Cl atoms positioned approximately equidistant above and below the plane of the carbon backbone, with the carbon-carbon distance being shorter in the transition state than in the reactant¹³.

The CF₃CHFCF₃ molecule differs by a CF₃ substituent from CF₃CHFCH₂Cl. Study of the CF₃CHFCF₃ system generated the same *meso*, *d*,*l*-CF₃CHFCHFCF₃ peaks identified in the CF₃CHFCH₂Cl system¹⁴. Computational investigation found that the carbon losing the F was more planar than the carbon losing the H, and that such a trend was applicable to other HF transition states¹⁵. The C-F out-of-ring bond was shorter in the transition state than the reactant or product, "suggesting that the fluorine substituents are donating electron density to C-F"¹⁵. The Carbon-Carbon transition state bond was exactly halfway between the product and the reactant¹⁵. A CF₃ group in replacement of an H was suggested to raise the threshold energy by 4 kcal/molecule, and an additional replacement raised the threshold energy an additional 2 kcal/mole¹⁵. Methyl substituents tended to decrease threshold energy, but this was a more pronounced effect when attached to the carbon with the fluorine¹⁵.

The study of the CH₃CHFCH₂Cl and CF₃CHFCH₂Cl system was undertaken in order to compare the influence of an electron donating substituent with an electron withdrawing substituent, with particular interest in the relative rate

of the HF versus HCl elimination channels and the F/Cl interchange pathway. The experimental rate constants will be compared to the calculated statistical unimolecular rate constants to assign experimental threshold energies.

2. Experimental

The CF₃CHFCH₂Cl* experiments consist of placing measured quantities of CH₂ClI and CF₃CHFI in Pyrex vessels of known volume followed by photolysis at room temperature with a high pressure 200 W mercury lamp (Oriel). The contents of the vessels were recovered and analyzed by gas chromatography using either flame-ionization or mass-spectrometric detectors. The ratio of CH₂ClI and CF₃CHFI was typically 1:4 and the normal time for photolysis was 10 minutes. A small quantity of solid mercury (I) iodide was added to each vessel to aid in the generation of radicals¹⁰⁻¹⁹. Gas handling was done on an all-glass, grease-free, high-vacuum line and pressures were measured with a MKS-270 electronic manometer.

Lower pressures were needed for the $CF_3CHFCH_2Cl^*$ system; therefore, large photolysis vessels ranging in size from 34.71 to 4900 cm³ were used. Commercial samples of all products were available except for the stabilized molecule and rearranged product, and identification of the gas chromatographic signals was straightforward. Mixtures of known composition were prepared to obtain calibration factors to convert the raw product ratios to ratios of actual concentrations. It was assumed that the total ion-count from the isomeric CF_3CFHCH_2Cl and $CF_3CHClCH_2F$ molecules were the same as CF_3CFHCH_2Cl to obtain the calibration factor for $CF_3CHClCH_2F$.

The rate constants for the CH₃CHFCH₂Cl* and CH₃CHClCH₂F* molecules are 2-3 orders of magnitude larger than for CF₃CHFCH₂Cl*, and correspondingly smaller vessels were used for photolysis. Since CH₃CHFI was not available, the experiments for the CH₃CHFCH₂Cl system utilized mercury photosensitization of CH₃CHFCl and CH₂ClI in quartz vessels to produce the CH₃CHF and CH₂Cl radicals, which in combination produced the desired CH₃CHFCH₂Cl* molecules. The CH₂=CHCl produced from the decomposition of CH₂ClCH₂Cl* formed from the recombination of the CH₂Cl radicals seemed to protect the alkenes from reaction with Cl-atoms, but in accordance with the procedure in similar Hg photosensisitation experiments an additional scavenger, $CF_3CH=CH_2$, which did not interfere with the analysis of any products, was used to protect the chloro- and fluoropropenes from Cl-atom reactions. The typical composition of a sample was 0.325 □mole CH₂CII, 0.650 □mole CH₃CHFCl and 0.244 □ mole CF₃CH=CH₂. Commercial samples of all the halogenated propense other than E- and Z-CH₃CH=CHF were available to enable identification of gas chromatograph peaks. Carefully prepared mixtures were used to obtain relative calibration factors for the chloro- and fluoropropenes, and it was assumed that CH₃CH=CHF would ionize in the same way as CH₃CF=CH₂. Commercial samples were unavailable for CH₃CHFCH₂Cl and CH₃CHClCH₂F. Identification of their gas chromatography peaks was possible from their mass spectra and the dependence of their relative yields with reduced pressure. Calibration factors for D_i/S ratios were obtained from the assumption that the ratio of the total ion-count for CH2=CHCl to the total ion-count for CH2FCH2Cl would the same as that for the CH₃CH=CHCl/CH₃CHFCH₂Cl ratio, and prepared mixtures of CH₂=CHCl and CH₂FCH₂Cl were used for calibration. Since parent-ion counts actually were used for the halopropenes, the ratio was then adjusted for the parent-ion component of $CH_2 = CHCl$ and $CH_3CH = CH_2Cl$ in the total-ion counts. In another approach, several photolyses were done with analysis by flame-ionization detection and the ratio of signals from the chloropropene and CH₃CHFCH₂Cl were measured. Based upon previous experience in this laboratory, the response of the FID for these compounds would be similar, i.e. the correction factor to obtain relative concentrations would be close to unity. These experiments confirmed the calibration based on the CH₂=CHCl/CH₂FCH₂Cl analogy.

Electronic structure calculations (Density-Functional Theory with the B3PW91 method and the 6-311+G(2d,p) basis set) were used to obtain the vibrational frequencies and moments of inertia of the molecules and the transition states. Calculations also were done with the 6-31G(d',p') basis set for comparison.

3. Results and Discussion

The vibrationally activated molecules (denoted by an asterisk) were generated in a room temperature bath gas (M) by the recombination of CH₂Cl radicals with CF₃CHF and CH₃CHF radicals that were formed by the photolysis of CH₂ICl with either CF₃CHFI or CH₃CHFCl. The pathways of reaction are identified by numbering the carbon atoms 1, 2 and 3 from left to right as the formulas are written. The CF₃CHFCH₂Cl^{*} molecules have three unimolecular reaction channels that are in competition with collisional deactivation, as outlined below; the fourth possibility, 2,1-HF elimination, was not observed due to the high threshold energy for this reaction.

$$\begin{array}{rcl} CF_{3}CHFCH_{2}Cl^{*} & \rightarrow & CF_{3}CHClCH_{2}F^{*} \\ & \rightarrow & HF + & CF_{3}CH=CHCl \ (cis \ and \ trans) \\ & \rightarrow & HCl + & CF_{3}CF=CH_{2} \\ & + & M & \rightarrow & CF_{3}CHFCH_{2}Cl + & M \end{array}$$
(1)

The important reactions for $CF_3CHClCH_2F^*$ are 2,3-HF and 3,2-HCl elimination. The reverse of the Cl/F-interchange step is a minor component, and it can be ignored in the analysis. As shown in (2), the reactions of $CH_3CHFCH_2Cl^*$ do include 1,2-HF elimination plus Cl/F-interchange and 3,2-HF and 2,3-HCl elimination.

$$\begin{array}{rcl} CH_{3}CHFCH_{2}Cl^{*} & \rightarrow & CH_{3}CHClCH_{2}F^{*} \\ & \rightarrow & HF + & CH_{2}=CFCH_{2}Cl \\ & \rightarrow & HF + & CH_{3}CH=CHCl \ (cis \ and \ trans \) \\ & \rightarrow & HCl + & CH_{3}CF=CH_{2} \\ & + & M & \rightarrow & CH_{3}CHFCH_{2}Cl + M \end{array}$$

$$(2)$$

The main reaction of $CH_3CHClCH_2F^*$ is 1,2-HCl and 3,2-HCl elimination, but some 2,3-HF elimination was observed. The experimental rate constants are obtained from measurements of the ratios of the relative concentrations of the decomposition product (D_i) for a specific channel, i, to the stabilized molecule (S) for a range of pressure. Product retention times for reactants and products in the CF_3CHFCH_2Cl system are shown below in Table 1. Figures 1-5 show the plotted data for the CH_3 and CF_3 systems.

Table 1. Retention times for CF₃CHFCH₂Cl system.

Product	Retention Time (s)
CF ₃ CF=CH ₂	6.17-6.36
CF ₃ CH=CHF	6.68
CF ₃ CHFCHF(meso)	9.34
CF ₃ CH=CHF	10.25
CH ₂ =CHCl	10.88
CF ₃ CCl=CH ₂	13.00
CF ₃ CHFCHF (d,l)	14.83
CF ₃ CH=CHCl	14.63
CF ₃ CHFCH ₂ Cl	26.14
CF ₃ CH=CHCl	26.87
CF ₃ CHClCH ₂ F	28.36
CF ₃ CHFI	30.97
CH ₂ ClI	50.78



Figure 1. Plots of product branching ratios from CH₃CHFH Cl* and vs. pressure⁻¹. \Box CH =CHCH₂Cl + (E+Z)-CH₃CH=CHCl/CH₃CF=CH₂•CH₂=CHCH₂Cl/CH₃CH=CHCl (E and Z) \Box CH₃CF=CH₂/CH₃CHClCH₂F+CH₂=CHCH₂F+(E+Z)-CH₃CH=CHF+CH₃CCl=CH₂• E/Z-CH₃CH=CHCl.



Plots of product branching ratios from CH₃CHClCH₂ $^{+}$ ^{*} vs. pressure⁻¹. \Box (E+Z-CH₃CH=CHF+CH₂FCH=CH₂)/CH₃CCl=CH₂ $^{-}$ CH₂FCH=CH₂/(Z+E-CH₃CH=CHF) • E/Z-CH₃CH=CHF



Plots of the decomposition to stabilization product ratios from CH₃CHFCH₂Cl^{*} vs. pressure⁻¹. \blacksquare (CH₂=CHCH₂Cl +(E+Z)-CH₃CH=CHCl)/CH₃CHFCH₂Cl \square CH₃CF=CH₂/CH₃CHFCH₂Cl \bullet CH₃CCl=CH₂/CH₃CHFCH₂Cl



1/P (Torr)

Figure 4. Plots of the decomposition to stabilization product ratios for CF₃CHFCH₂Cl* vs. pressure⁻¹; CF₃CF=CH₂/CF₃CHFCH₂Cl, □-E- and Z-CF₃CH=CHCl/CF₃CHFCH₂C; ■- (CF₃CCl=CH₂ + E- and Z-CF₃CH=CHF + CF₃CHClCH₂F)/CF₃CHFCH₂Cl. The lines are least-square fits to the data points. The correlation coefficients are between 0.96 and 0.93 and the intercepts are effectively zero.



Figure 4. Plots of the decomposition to stabilization product ratios for $CF_3CHClCH_2F^*$ vs. pressure⁻¹. \Box -CF₃CCl=CH₂/CF₃CHClCH₂F, •- E +Z- CF₃CH=CHF/CF₃CHClCH₂F. The lines are least-square fits to the data points; the correlation coefficients are 0.92(upper line) and 0.56(lower line). In spite of the scatter of the data for HCl elimination, the branching ratio based on the rate constants is in good agreement with the ratio from Figure 3.

The energy profiles of the reactions for the CF_3CHFCH_2Cl and CH_3CHFCH_2Cl systems are summarized in Table 2. The Cl/F interchange reactions are just slightly endothermic. The calculated threshold energies from both basis sets are listed in Table 2; the experimentally assigned values are given in Table 3. The CF_3CHFCH_2Cl system differs from previously studied systems in that HCl elimination does not dominate as the fastest elimination channel. The interchange product was experimentally detected, identifiable in the GC-MS Chromatograph and confirmed by the identification of products only producible by elimination from the interchange molecule, $CF_3CHClCH_2F$. The most striking result for the CH_2FCD_2Cl , CF_3CHFCH_2Cl , and CH_3CHFCH_2Cl series is the similarity of the branching fraction for the Cl/F interchange reaction, which is approximately 0.18 for all three cases. Thus, whatever the nature of the substituent effect, it seems to affect the interchange reaction and the HX-elimination reactions in a similar way. The experimentally assigned threshold energies are 62, 64 and 56 kcal mol⁻¹ for

CH₂FCD₂Cl, CF₃CHFCH₂Cl, and CH₃CHFCH₂Cl, respectively, which follows the trend from the DFT calculations illustrated in Table 3.

Evidently the CF₃ group increases the threshold energy (E₀) for Cl/F interchange, whereas the CH₃ group lowers E₀. Furthermore, the effect is more pronounced for CH₃ than for CF₃. These trends are in accord with expectations for the effects of electron-releasing and electron-withdrawing groups on the threshold energies of dyotropic rearrangement reactions involving halogen atoms^{20,21}. The CF₃ and CH₃ groups do distort the geometry of the bridged transition state without changing the C-C distance appreciably, as illustrated in Figure 1. The C-F and C-Cl distances closer to the C(H)(CF₃ or CH₃) end are lengthened, and the halogen atoms are displaced slightly toward the CH₂ end of the structure. This effect is more noticeable for the CH₃ group than for the CF₃ group. The initial discovery¹² of the Cl/F interchange reaction was with the CF₂ClCF₂CH₃ molecule, which had the benefit of the effect of the CH₃ group, but the unfavorable effect associated with a F-atom on the methyl carbon, and E₀ was¹³ 67 kcal mol⁻¹.

Table 2 Experimental Rate Constants^a

Reaction	CF ₃ CHFCH ₂ Cl ^b	CF ₃ CHClCH ₂ F ^b	CH ₃ CHFCH ₂ Cl ^c	CH ₃ CHClCH ₂ F ^c
	10^{-3} Torr	10^{-3} Torr	Torr	Torr
	10^4 s^{-1}	10^4 s^{-1}	10^7 s^{-1}	10^7 s^{-1}
3,2-Cl/F	0.96 ± 0.1		0.47 ± 0.05	
	1.3 ± 0.2		0.70 ± 0.08	
2,3-HCl	2.4 ± 0.1		0.25 ± 0.02	
	3.4 ± 0.4		0.39±0.30	
3,2-HCl		0.72 ± 0.32		0.76 ± 0.10
		1.0 ± 0.4^{d}		1.1 ± 0.2^{e}
3,2-HF	1.5 ± 0.1		0.67 ± 0.05	
	2.1 ± 0.2^{d}		1.0 ± 0.1^{e}	
2,3-HF		4.2 ± 0.5		0.038 ± 0.005 .
		5.9 ± 0.7		0.057 ± 0.007
1,2-HF	(f)	(f)	1.01 ± 0.09	
			1.5 ± 0.2	
1,2-HCl				2.1 ± 0.3
				3.2 ± 0.4

a. The top entry lists the slopes obtained from the plots of D/S vs. pressure⁻¹ and immediately under the slope is the rate constants in s^{-1} units.

b. The following collision diameters (cm) and ϵ/k (°K) were used to calculate the collision constant; CF₃CHFCH₂Cl (5.6 x 10⁻⁸ and 410), CF₃CHFI (5.3 x 10⁻⁸ and 300), CH₂ClI (5.1 x 10⁻⁸ and 400). The collision frequency for CF₃CHFCH₂Cl* was 1.4 x 10⁷ s⁻¹/Torr. The same value was used for CF₃CHClCH₂F*.

c. The following collision diameters (cm) and ϵ/k (°K) were used to calculate the collision constant; CH₃CHFCH₂Cl (5.5 x 10⁻⁸ and 350), CF₃CHFI (5.3 x 10⁻⁸ and 300), CH₂ClI (5.1 x 10⁻⁸ and 400). The collision frequency for CH₃CHFCH₂Cl* was 1.5 x 10⁷ s⁻¹/Torr. The same value was used for CH₃CHClCH2F.

d. The *trans/cis* ratios for CF₃CH=CHCl and CF₃CH=CHF were 3.1 and 1.5, respectively.

e. The *trans/cis* ratios for CH₃CH=CHCl and CH₃CH=CHF were 0.66 and 0.60, respectively.

f. The E_0 for 2,1-HF elimination from CF₃CHFCH₂Cl and CF₃CHClCH₂F is expected to be higher than 70 kcal mol¹, and this reaction is not competitive with the observed elimination reactions.

Table 3 Assignment of threshold energies. The theoretical values are usually lower than the experimental values for HCl elimination and Cl/F-interchange processes.

Table 1	3.
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Process	<e> kcal/mol</e>	kexpt S-1	k <e> S-1</e>	Eo kcal/mol
CF ₃ CHFCH ₂ Cl*	90		·	
3,2-Cl/F		1.3 x 104	1.4 x 104	64 ± 2
2,3-HCl		3.4 x 104	4.2 x 104	64 ± 2
3,2-HF		2.1 x 104	2.2 x 104	65 ± 2b
CF3CHClCH2F*	88			
2,3-HF		5.9 x 104	6.0 x 104	61 ± 2
3,2-HCl		1.0 x 104	0.92 x 104	67 ± 3
CH3CHFCH2Cl*	92			
3,2-Cl/F		0.70 x 107	0.72 x 107	$56 \pm 3c$
2,3-HCl		0.38 x 107	0.48 x 107	60 ± 3
1,2-HF		1.5 x 107	1.5 x 107	58 ± 3
3,2-HF		1.0 x 107	1.0 x 107	58 ± 3
CH3CHClCH2F*	91			
1,2-HCl		3.2 x 107	2.6 x 10 7	$58 \pm 3c$
3,2-HCl		1.1 x 107	1.0 x 107	59 ± 3
2,3-HF		0.057 x 107	0.052 x 107	62 ± 3
CH ₂ FCH ₂ Cl*(a)	91			
2,1-Cl/F		0.40 x 108	0.62 x 108	62 ± 3
1,2-HCl		0.82 x 108	1.4 x 108	65 ± 2
2,1-HF		1.1 x 108	1.3 x 108	63 ± 2

a) The E_0 for the interchange rate constant is from the study of CH_2FCD_2Cl in reference 16.

The E_0 for the elimination reactions are from reference 15.

b) This value was assigned by using the sum of rate constants for the *cis*- and *trans*- isomers. If the E_0 are assigned separately, the values would be 64.5 (*trans*) and 66.0 (*cis*) kcal mol⁻¹.

c)The large uncertainty is associated with the difficulty in the calibration for the relative concentrations of CH_3CHFCH_2Cl and $CH_3CHClCH_2F$, see text.

4. Conclusion

The influence of the CF₃ and CH₃ groups on the threshold energies of the dyotropic halogen- atom rearrangement reaction has been measured for vibrationally activated CF₃CHFCH₂Cl and CH₃CHFCH₂Cl molecules. The threshold energies are 64 and 56 kcal mol⁻¹; the CF₃ group raises and the CH₃ lowers the threshold energy relative to CH₂FCD₂Cl (E₀ = 62 kcal mol⁻¹). The DFT calculations with the B3PW91 method also support this trend for the threshold energies. Based upon these two examples and other electronic structure calculations²⁰⁻²², electron-density donating groups lower the threshold energy and electron-density withdrawing groups raise the threshold energy for the unimolecular halogen-atom interchange reaction. The HF and HCl elimination reactions in the CF₃CHFCH₂Cl and CH₃CHFCH₂Cl systems are in competition with the rearrangement reaction, and rate constants also were measured for these unimolecular reactions. The branching fraction for rearrangement was nearly constant, 0.18 ±0.03, in the these systems, as well as for CH₂FCD₂Cl, and the substituents affect the elimination and rearrangement reactions is similar ways. In particular, the electron-density releasing character of the CH₂Cl and CH₂F groups is nearly as strong as for the CH₃ group in promoting HF elimination from CH₃CHFCH₂Cl and HCl elimination.

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