Substituent Effects and Threshold Energies for the Unimolecular Elimination of HCl (DCl) and HF (DF) from Chemically Activated CFCl₂CH₃ and CFCl₂CD₃

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Combination of CFCl₂ and methyl- d_0 and $-d_3$ radicals form CFCl₂CH₃- d_0 and $-d_3$ with 100 and 101 kcal/mol of internal energy, respectively. An upper limit for the rate constant ratio of disproportionation to combination, k_d/k_c , for Cl transfer is 0.07 ± 0.03 for collision of two CFCl₂ radicals and 0.015 ± 0.005 for CH₃ and CFCl₂ radicals. The chemically activated CFCl₂CH₃ undergoes 1,2-dehydrochlorination and 1,2-dehydrofluorination with rate constants of 3.9×10^9 and 4.9×10^7 s⁻¹, respectively. For CFCl₂CD₃ the rate constants are 8.7 × 10^8 s⁻¹ for loss of DCl and 1.1×10^7 s⁻¹ for DF. The kinetic isotope effect is 4.4 ± 0.9 for HCl/DCl and appears to be identical for HF/DF. Threshold energies are 54 kcal/mol for loss of HCl and 68 kcal/mol for HF; the E_0 's for the deuterated channels are 1.4 kcal/mol higher. Comparison of these threshold energies with other haloethanes suggests that for HF and HCl elimination the transition states are developing charges of different signs on the carbon containing the departing halogen and that chlorine and fluorine substituents exert similar inductive effects.

Introduction

Two of the classic mechanisms in organic chemistry^{1,2} are E_1 and E_2 eliminations of a hydrogen halide from a haloalkane. The transition state for first order eliminations, E₁, involves heterolytic fission of the carbon-halogen bond and formation of a planar carbocation. The second order elimination mechanism, E₂, is assisted by a base and involves a planar transition state with an anti-configuration; i.e., the halogen and hydrogen are removed from opposite sides of the C-C bond. In the gas phase, the 1,2-dehydrohalogenation reaction has been assumed^{3,4} to involve a planar and polar four-centered transition state, and it has been shown⁵ that syn-elimination governs the removal of the hydrogen halide. For the past 3 decades³⁻⁸ experiments have been designed to better understand the polarity of the 1,2dehydrohalogenation transition state, primarily by measuring the effect of different substituents on the rate constant and on the threshold energy barrier, E_0 . Most of the experimental work⁵⁻⁷ has involved chloro- and fluoroalkanes because complicated reaction chemistry can result from carbon-halogen bond rupture with bromo- and iodoalkanes.

For chloroethanes the effect of chlorine substituents at the α -carbon (the carbon containing the halogen) for the unimolecular elimination of HCl is a decrease of 2–3 kcal/mol in E_0 (HCl) for successive replacement of hydrogen by chlorine.⁶ For fluoroethanes the effect of fluorine substituents at the α -carbon is an increase of E_0 (HF) by 3 kcal/mol when one α -hydrogen of fluoroethane is replaced by a fluorine.⁶ Substitution of the second α -hydrogen with fluorine results in an additional 7 kcal/mol increase in E_0 (HF).⁶

It has been suggested^{3,4,6} that the threshold energies for the removal of HF from fluoroethanes exhibit trends opposite that for loss of HCl from chloroethanes because the Cl and F substituents exert different electronic effects on common transition states. Specifically, the charge on the α -carbon becomes more positive, and a partial negative charge develops on the carbon containing the hydrogen, the β -carbon. The decrease in E_0 (HCl)'s with successive Cl substitution is explained^{3,4} by resonance stabilization as a lone pair of the

chlorine is delocalized to the developing positive charge on the α -carbon. A fluorine substituent's high electronegativity is thought^{3,4,6} to destabilize the transition state by inductive withdrawal of electron density from the α -carbon, increasing the E_0 with sequential fluorine substitution.

Unimolecular rate constants7 measured for elimination of HF and HCl from chemically activated CF_2ClCH_3 produced E_0 's inconsistent with the idea of common transition states and different electronic effects for Cl and F substituents. For CF2-ClCH₃, the chlorine and fluorine substituents had the same effect on E_0 when HF was eliminated. Both substituents increased $E_0(HF)$ so that E_0 's for CF₃CH₃ (68 kcal/mol) and CF₂ClCH₃ (69.5 kcal/mol) are nearly identical. We should note that the uncertainity in experimental threshold energies is normally 2 kcal/mol. For HCl elimination, fluorine substituents behave like hydrogens; the threshold energies are identical at 55 kcal/mol for both CH₂ClCH₃ and CF₂ClCH₃. To account for the behavior of the chlorine substituents on $E_0(HF)$ and the fluorine substituents on E_0 (HCl), we suggested⁷ that the transition states have different polarity and that Cl and F substituents exhibit similar electronic effects; i.e., both either accept or donate electron density to the carbon skeleton.

Recently, Toto et al.9 reported ab initio quantum chemical calculations designed to determine the geometry, bond orders, atomic charges, and activation energies for the transition states for 1,2-HX elimination (X = F, Cl, Br, and I) from haloethanes. Theoretical results will be an important aid in understanding this class of reactions because of the ambiguous nature of halogen substituent effects. In general, these calculations predicted a very asymmetric transition state structure with bond orders that are much stronger for C-C and C-H and much weaker for C-X and H-X than previous models.^{6,10-12} The calculated C-H and C-X bond orders and their relation to the experimental kinetic isotope effect will be considered in the Results and Discussion. For fluoroethane the calculated activation energy was within the experimental uncertainty, but the $E_{\rm a}$'s were generally 3–7 kcal/mol too high for all the haloethanes. Identical E_a 's were predicted for HF and HCl and for HBr and HI, contrary to observations.⁹

Transition states for loss of HF and HCl were also computed

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for all possible α -chloro-/fluoro-substituted ethanes to explore the substituent effects and the transition states' ionic character. Theoretical activation energies agreed with the experimentally observed increase in Ea for HF elimination with increasing α -substitution but a decrease in E_a for HCl elimination. For CF_2ClCH_3 a calculated difference in $E_0(HF)$ and $E_0(HCl)$ of 10.4 kcal/mol is close to the experimental⁷ difference of 14.5 kcal/mol. Two important findings of the calculations9 are that (1) for elimination of either HCl or HF, the transition state geometry, bond orders, and atomic charges are nearly independent of substituents but (2) the bond orders and the developing atomic charges for the HF and HCl elimination transition states are considerably different. The former supports our use of identical Arrhenius A-factors to develop common transition state models for the RRKM calculations, regardless of the substituents on the α -carbon. The latter point supports our contention⁷ that different transition states exist for loss of HF and HCl. Results and Discussion will consider the calculated atomic charges and the substituent effects in greater depth.

This work will further test the effect of Cl and F substituents on the E_0 's for competitive 1,2-HF and 1,2-HCl eliminations by preparing chemically activated CFCl₂CH₃ and measuring the unimolecular rate constants. Threshold energies for HF and HCl elimination will be obtained by matching the experimental rate constants to rate constants calculated using the RRKM theory. Comparison of these threshold energies to other halosubstituted ethanes and to the predictions of Toto *et al.*⁹ should provide additional information about the nature of halogen substituents and the polar character of the transition states. The deuterated analogue, CFCl₂CD₃, was also studied to obtain the kinetic isotope effect.

Chemically activated CFCl₂CH₃ (CFCl₂CD₃) is formed with 100 (101) kcal/mol of energy by combination of CFCl₂ and CH₃ (CD₃) radicals. These radicals are generated by the photolysis of 1,2-difluoro-1,1,2,2-tetrachloroacetone and acetone- d_0 (- d_6). The following scheme summarizes the reactions expected for this system, with the deuterated channels omitted. The asterisk denotes a chemically energized species.

$$(CFCl_2)_2CO \xrightarrow{\mu\nu} 2CFCl_2 + CO$$
 (1a)

$$\xrightarrow{m\nu} \text{Cl} + \text{CFCl}_2\text{COCFCl} \quad (1b)$$

$$CH_3 + CH_3 \rightarrow CH_3 CH_3$$
 (2)

$$CFCl_2 + CH_3 \xrightarrow{k_d} :CFCl + CH_3Cl$$
 (3a)

$$\xrightarrow{\kappa_c} CFCl_2CH_3^* \tag{3b}$$

$$CFCl_2 + CFCl_2 \xrightarrow{k_d} :CFCl + CFCl_3$$
 (4a)

$$\xrightarrow{\kappa_{c}} CFCl_2 CFCl_2^* \qquad (4b)$$

The fate of the :CFCl carbene may be dimerization to CFCl=CFCl, similar to the reactions of the :CF₂ carbene,⁷ or it may be removed by reactions with the CFCl₂ or CH₃ radicals. Reactions 3a and 4a are disproportionations, transferring a Cl from CFCl₂ to CH₃ and to CFCl₂, respectively. The combination reactions (3b and 4b) form the chemically activated species. These rate constant ratios, k_d/k_c , will be reported. Photoactivated difluorotetrachloroacetone reacts either by breaking the C-C (1a) or the C-Cl bond (1b).¹³ Rupture of the C-Cl bond increases in importance with increasing number of Cl substit-

uents on haloacetones¹⁴ and with wavelengths shorter than 313 nm.¹⁵ Chlorine radicals from reaction 1b will react with alkenes produced by the loss of HCl and HF from the CFCl₂CH₃* (reactions 5a and 5b) which would give unimolecular rate constants that are too small. Atomic chlorine has been observed to react with alkenes in similar chemical activation systems,¹⁶ and propene was an efficient competitor for its removal. Therefore, a narrow band pass filter centered at 313 nm was used to reduce the undesired C–Cl fission, and a scavenger of propene was also used to protect the alkene products.

The CFCl₂CH₃* can undergo loss of HCl and HF or become stabilized through collision (reactions 5a-c). The ratio of the yield of the decomposition (*D*) product from reaction 5a and 5b and the stabilization (*S*) product yield, CFCl₂CH₃, plotted

$$CFCl_2CH_3^* \xrightarrow{k_{HCl}} CFCl = CH_2 + HCl$$
 (5a)

$$\xrightarrow{k_{\rm HF}} {\rm CCl}_2 = {\rm CH}_2 + {\rm HF}$$
 (5b)

$$\xrightarrow{k_{\rm M}[{\rm M}]} {\rm CFCl}_2{\rm CH}_3 \tag{5c}$$

versus inverse pressure should produce a linear relationship at higher pressures with a zero intercept. The experimental rate constant, k_a , equals $k_M[M](D/S)$, where $k_M[M]$ is the collision rate. It is anticipated that $k_{HCl} \gg k_{HF}$ so that when the yield of $CCl_2=CH_2$ is measurable, the yield of $CFCl_2CH_3$ would be too small to be observed; thus, only k_{HCl} can be determined from a plot of D/S versus inverse pressure. To obtain k_{HF} , the branching ratio of k_{HCl}/k_{HF} will be obtained from a plot of $[CFCl=CH_2]/$ $[CCl_2=CH_2]$ versus inverse pressure using data collected at very low pressures, where the yields of $CFCl=CH_2$ and $CCl_2=CH_2$ are the greatest. Similar plots constructed for the deuterated molecule will provide k_{DCl} , k_{DF} , and the deuterium kinetic isotope effect.

Experimental Section

Quartz vessels with a volume range of 17.13–992.3 cm³ containing 2.23 µmol of 1,1-difluoro-1,1,2,2-tetrachloroacetone, 30.1 µmol of acetone or deuterated acetone, 0.94 µmol of propene, and a bath gas of 1.04 mmol of sulfur hexafluoride were photolyzed using a high-pressure Oriel 6137 mercury lamp and an Oriel 59154 narrow-band-pass filter centered at 313 nm. For 30 min photolyses at room temperature, the typical reactant conversion rates were less than 5%. Lower pressure mixtures devoid of SF₆ and propene were required to measure the HCl/ HF branching ratio. All samples were prepared on a greasefree vacuum line using an MKS 270 electronic manometer. A Shimadzu 14A FID GC with a 1/8 in. stainless steel column containing Hayesep A coated with nickel that had been reduced by H₂ from a 5.0% NiCl₂ solution was used for analyses. Using an initial temperature of 100 °C for 5 min followed by temperature programming at 1 °C/min to a final temperature of 167 °C, the elution times (in minutes) were generally as follows: SF₆, 0.1 min; C₂H₆, 2; propene, 7; CH₃Cl, 12; CFCl=CH₂, 13; CFCl₂H, 37; CFCl₃, 40; CCl₂=CH₂, 43; CFCl₂-CH₃, 49; acetone, 67; CFCl₂CFCl₂, 128; difluorotetrachloroacetone, 325. The data were collected and integrated with a Shimadzu Chromatopac CR5A integrator.

Products were identified by comparison of GC retention times with commercial samples and verified by a Hewlett-Packard 5890/5791 GC/MS equipped with a 50 m PONA capillary column. The CCl₂=CH₂ could not be identified by mass spectrometry due to its very low yield, but the CFCl=CH₂,



Figure 1. Plot of $[CFCl_3]/[CFCl_2CFCl_2]$ versus the log of reciprocal pressure. The product ratio is k_d/k_c . The circles are for photolysis of 1,2-dichloro-1,1,2,2-tetrafluoroacetone with acetone- d_0 , and the squares are with acetone- d_6 . Decomposition of chemically activated CFCl₂-CFCl₂ may cause the upward curvature at lower pressures; see Results and Discussion.

CCl₂=CH₂, and CFCl₂CH₃ did exhibit the expected pressure dependence of a chemically activated, unimolecular decomposition system.

Relative calibration factors, which are needed for D/S, HCl/ HF branching ratios, and k_d/k_c , were measured as [CFCl=CH₂]/ $[CFCl_2CH_3] = 0.747, [CFCl=CH_2]/[CCl_2=CH_2] = 1.15, [CFCl_3]/$ CH_3] = 2.1. These relative responses were determined using six to eight trials of three mixtures prepared to replicate typical reaction yields and GC elution characteristics. Calibration factors for the deuterated system were assumed to be the same as the undeuterated compounds. Our response factors are consistent with observations by Tschuikow-Roux et al. in that increasingly halogenated methanes and ethanes exhibit reduced response.¹⁷ Calibration factors vary^{18,19} with alteration of hydrogen and air flame conditions; therefore, the response factors reported here may not be applicable for other work. We have also found²⁰ that response factors for halocarbons, unlike those for hydrocarbons, vary dramatically with small variations in the fuel/air ratios.

Results and Discussion

1. Disproportionation/Combination Rate Constant Ratios. Two disproportionation/combination rate constant ratios (k_d/k_c) can be determined from the product yields. The k_d/k_c 's will be upper limits because the disproportionation product could also be formed by radicals abstracting Cl from difluorotetrachloroacetone. For collision of two CFCl₂ radicals, the $k_d/k_c = k_{4a}/k_{4b} = [CFCl_3]/[CFCl_2CFCl_2*]$ and is constant at 0.07 ± 0.03 in the pressure range from 1730 to about 10 Torr but clearly increases at lower pressures, Figure 1. Because the combination product is itself chemically activated, CFCl_2CFCl_2* may react at lower pressures; presumably C–Cl bond rupture is the pathway with the lowest energy barrier, reactions 6a and 6b.

$$\operatorname{CFCl}_2\operatorname{CFCl}_2^* \xrightarrow{k_{\operatorname{Cl}}} \operatorname{CFCl}_2\operatorname{CFCl} + \operatorname{Cl}$$
 (6a)

$$\xrightarrow{k_{M}[M]} CFCl_{2}CFCl_{2}$$
(6b)

Reaction 6a would cause [CFCl₃]/[CFCl₂CFCl₂] to increase as pressure is reduced, and k_d/k_c doubles when half of the CFCl₂-CFCl₂* reacts, i.e., when $k_{Cl} = k_{M}$ [M]. RRKM theory was used to calculate k_{Cl} ; k_{M} was obtained from collision theory, and these gave [M], the pressure, when k_d/k_c doubled. Vibrational frequencies for CFCl₂CFCl₂ were estimated from CFCl₂CH₃.²¹ The transition state model used 5.0 as the moments of inertia

ratio, a C-Cl stretch was the reaction coordinate, and two C-C-Cl bends were reduced to 35 cm⁻¹; this gave 1.0×10^{16} s^{-1} as the Arrhenius A-factor at 1000 K.²² The threshold energy for C-Cl bond rupture for CFCl₂CFCl₂ is not known, so we tested four E_0 's (70, 75, 80, and 85 kcal/mol) that encompass the range in the reported C-Cl bond dissociation energies for CF_2Cl_2 (71.3-85 kcal/mol).²³ Assuming $k_M = 1.0 \times 10^7 \text{ Torr}^{-1}$ s⁻¹ and an average energy of 100 kcal/mol for CFCl₂CFCl₂*, the pressure when half of the CFCl₂CFCl₂* reacts is calculated to be 60 Torr ($E_0 = 70$ kcal/mol), 7 Torr ($E_0 = 75$ kcal/mol), 0.5 Torr ($E_0 = 80$ kcal/mol), and 0.03 Torr ($E_0 = 85$ kcal/ mol). Figure 1 shows that $k_d/k_c = 0.07$ at higher pressures and doubles between 1 and 10 Torr. The RRKM results are consistent with unimolecular decomposition of CFCl₂CFCl₂*, causing the increase in k_d/k_c at lower pressures if the C–Cl bond dissociation energy for CFCl₂CFCl₂ is between 70 and 80 kcal/ mol.

The other disproportionation/combination ratio that can be determined is for the collision of CFCl₂ and CH₃ radicals; $k_d/k_c = k_{3a}/k_{3b} = [CH_3Cl]/[CFCl_2CH_3*]$ and $[CFCl_2CH_3*] = [CFCl_2-CH_3] + [CFCl=CH_2] + [CCl_2=CH_2]$. On the basis of 47 trials, the k_d/k_c is independent of pressure and is constant at 0.015 \pm 0.005.

Substituents should influence the k_d/k_c 's, so determining the effect of F or Cl substituents for these bimolecular processes might assist in interpreting these effects for the unimolecular 1,2-HX elimination reactions. Molecular orbital theory (MYFF model),²⁴ applied to the transfer of an H from C₂H₅ radicals to methyl radicals, predicts that the transition state for disproportionation has ionic character, while it is neutral for combination. Thus, the disproportionation reaction rate constant, but not the combination rate, would be influenced by the electronic character of substituents. Further, this model suggests that electron withdrawing groups on the acceptor radical or electron donating groups on the donor radical both cause an increase in $k_{\rm d}$. In comparing a series of radical reactions, both $k_{\rm c}$ and $k_{\rm d}$ cause a variation in k_d/k_c . Analysis of the substituent effects of different halogens on k_c compared to those on k_d/k_c allows determination of the effects on $k_{\rm d}$. At room temperature, the most reliable k_c measurements show a decline in k_c 's with increasing halogenation with Cl's have a greater effect than fluorine: $3.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for CH₃ radicals,²⁵ 1.4×10^{10} M^{-1} s⁻¹ for CF₃ radicals,²⁶ and 0.2 × 10¹⁰ M⁻¹ s⁻¹ for CCl₃ radicals.27

We will now consider substituent effects on k_d/k_c and use the MYFF model and the trends in k_c to determine the effect of Cl and F substituents on k_d . Three sets of disproportionation/ combination reactions involving transfer of a chlorine between halomethyl radicals will be discussed. The first compares CH₃ + CClF₂ ($k_d/k_c = 0.24$ per transferable Cl)⁷ with CH₃ + CCl₂F $(k_d/k_c = 0.0075$ per transferable Cl). It should be noted that $k_d/k_c = 0.24 \pm 0.05$ for CH₃ + CClF₂ was considered tentative⁷ due to experimental complications. The radical listed first, methyl, is the acceptor and the second, differing by a chlorine and a fluorine, is the donor radical. The additional Cl when CCl_2F is the donor radical should reduce k_c , causing k_d/k_c to increase; however, it declines by a factor of 30. According to the MYFF model, a donor radical would reduce k_d if electron withdrawing groups were present; for CCl₂F to decrease k_d/k_c compared to CCIF₂, the Cl would have to be more strongly electron withdrawing than F. Secondly, substituent effects on the acceptor radical can be probed by comparing $CH_3 + CCl_2F$ $(k_d/k_c = 0.0075 \text{ per transferable Cl})$ with $CCl_2F + CCl_2F (k_d/k_c)$ = 0.0175 per transferable Cl), where the donor radical is constant and the acceptor radical changes from CH₃ to CCl₂F.



Figure 2. D/S versus reciprocal pressure plot for the four-centered elimination of HCl from CFCl₂CH₃ (circles) and elimination of DCl from CFCl₂CD₃ (squares). D is [CFCl=CH₂- d_0 and - d_2], and S is [CFCl₂CH₃- d_0 and - d_3], respectively.

Again, the increase in the number of halogen substituents (in this case on the acceptor radical) should reduce k_c , causing an increase for k_d/k_c . The k_d/k_c is a factor of 2 larger with CCl₂F versus CH₃ as the acceptor radical, consistent with electron withdrawing groups assisting the disproportionation reaction. However, a decline in k_c , an increase in k_d , or a decline in k_c that is larger than the decline in k_d could be responsible for the small increase in k_d/k_c . A final comparison shows trends in $k_{\rm d}/k_{\rm c}$ counter to the previous set. For this case the acceptor radical changes from CH₃ to CF₂Cl with the same donor radical, CF₂Cl. Comparing CH₃ + CClF₂ ($k_d/k_c = 0.24$ per transferable Cl)⁷ with CClF₂ + CClF₂ ($k_d/k_c = 0.085$)⁷, the additional halogens should decrease k_c and increase k_d/k_c , but the rate constant ratio declines by almost a factor of 3. In summary, it appears that no clear trend emerges for the effect of Cl and F substituents for disproportionation reactions, perhaps because the MYFF model should not be applied to the disproportionation reactions involving Cl transfer or to reactions that yield a carbene (reactions 3a and 4a) rather than an alkene. It is also possible that thermodynamic rather than kinetic factors determine the product distribution or that the MYFF model does not accurately represent disproportionation reactions.

2. Experimental Unimolecular Rate Constants. Photolysis of fluorinated acetones have been a useful precursor for fluoromethyl radicals,²⁸⁻³⁰ but chloroacetones are impractical because C-Cl bond rupture competes with the desired carboncarbon bond fission.^{14,31} Difluorotetrachloroacetone has rarely been used to generate CFCl₂ radicals³² for kinetic studies; although, we found it to be an effective source for CFCl₂ radicals despite production of Cl atoms. In our system, the Cl radicals attack the alkenes formed in reactions 5a and 5b, apparently decreasing the unimolecular rate constants. Propene was used to scavenge atomic chlorine;¹⁶ as it was added at a constant total pressure of 1000 Torr, the D/S increased from 0.19 with no propene, to become constant at 0.44 when the propene to total acetones ratio was 1:9. Maximum inhibition of the mechanism of radical attack was assumed. Some alkene may still be removed by reaction with atomic Cl; therefore, the rate constants are considered to be lower limits, and the E_0 's represent upper limits. In the kinetic runs, a smaller amount of propene was used because it was not completely resolved from CFCl=CH₂ in the GC analysis at higher propene concentrations.

The unimolecular rate constants for loss of HCl and DCl were determined from standard D/S plots; Figure 2 has a slope of 363 Torr for HCl and 81 Torr for DCl. Using temperature



Figure 3. Experimental yield of $[CFCl=CH_2]/[CCl_2=CH_2]$ (circles) and $[CFCl=CD_2]/[CCl_2=CD_2]$ (squares) versus reciprocal pressure. The difficulty of measuring the very small $CCl_2=CH_2$ or $CCl_2=CD_2$ yield is responsible for the scatter at higher pressures.

independent collision diameters of 5.9 Å (SF₆), 5.0 Å (acetone), 6.0 Å (difluorotetrachloroacetone), 4.0 Å (propene), and 5.7 Å (CFCl₂CH₃), the $k_{\rm M}$ was 1.07×10^7 Torr⁻¹ s⁻¹ and gave $k_{\rm HCl}$ = 3.9×10^9 s⁻¹ and $k_{\rm DCl}$ = 8.7×10^8 s⁻¹. Collision diameters, assumed invariant with deuterium substitution, are known³³ for SF₆, acetone, and propene and were estimated for difluorotetrachloroacetone and CFCl₂CH₃ by comparison to analogous molecules.³³ The rate constants for loss of HF, 4.9×10^7 s⁻¹, and DF, 1.1×10^7 s⁻¹, were determined from the HCl/HF branching ratio of 80 in the low-pressure region, Figure 3.

Considerable scatter exists in Figure 3 due to the difficulty in measuring the very small yield of CCl₂=CH₂. The intercepts for the D/S plots of Figure 2 are negative for both the CFCl₂-CH₃ and the CFCl₂CD₃ systems. Causes for this deviation could include inaccurate measurements of the pressures, incorrect calibration response factors for the flame ionization detector, or an error in the product yields for CFCl=CH₂ or CFCl₂CH₃. An MKS electronic manometer with a reported uncertainty of 0.08% was used in pressure measurements. The pressures would have to be adjusted by over 100 Torr to give a zero intercept. This corresponds to greater than 10% variation from most pressures and, thus, cannot be the source of this error.

Alternate calibration factors were also tested to determine the value that would produce a zero intercept. Modifying the calibration factors changed the slope but only slightly altered the intercept; for example, reducing the calibration factors by 10% increased the intercept from -0.016 to -0.014, while the slope decreased by about 10%. Increasing the calibration factor by 10% decreased the intercept from -0.016 to -0.017 and the slope increased by about 11%. The calibration factor would have to be in error by at least a factor of 2 to produce an intercept close to zero. The actual [CFCl=CH₂]/[CFCl₂CH₃] calibration factor was 0.630 with 1 standard deviation being 0.051. Because reasonable adjustments in the calibration factor did not give significant improvement, an inaccurate response factor is not responsible for the nonzero intercepts.

A final explanation would be the loss of some of the decomposition product, excess $CFCl_2CH_3$, or incorrect measurements of their yields. The integration for the $CFCl=CH_2$ peak area was the least reliable because the GC analysis did not completely resolve it from the very large propene peak. This was particularly problematic at the highest pressures, where the yield of $CFCl=CH_2$ approached zero. The $CFCl=CH_2$ yield could also be low due to its removal by chlorine atoms. A typical $CFCl=CH_2$ peak area from the digital integrator was 50 000 counts for higher pressures and over 100 000 counts for lower pressures. For chemically activated $CFCl_2CH_3^*$, addition

TABLE 1: Summary of Experimental Rate Constants and RRKM Models for 1,1-Dichloro-1-fluoroethane

	molecules		activated complexes, elimination of			
	CFCl ₂ CH ₃	CFCl ₂ CD ₃	HCl	DCl	HF	DF
vibr freq, cm ⁻¹ (degeneracies)	2998 (3)	2246 (3)	2991 (2)	2227 (2)	2991 (2)	2227 (2)
	1423 (3)	1021 (5)	1478 (2)	1223 (3)	1452 (3)	1481 (2)
	1070 (4)	818 (3)	1123 (3)	925 (2)	1048 (3)	904 (4)
	750(1)	591 (1)	823 (4)	774 (2)	794 (2)	543 (4)
	591 (1)	403 (3)	610(1)	457 (3)	571 (3)	389 (2)
	403 (3)	276 (2)	403 (3)	389 (2)	389 (2)	304 (2)
	$266(3)^a$	150(1)	317 (2)	345 (3)	277 (2)	264 (1)
moments of inertia, I^{\ddagger}/I			0.955	0.955	0.970	0.970
reaction path degeneracy ^a			4	4	2	2
preexponential factor, ^b s ⁻¹			7.0×10^{12}	8.5×10^{12}	9×10^{12}	11×10^{12}
E_0 , kcal/mol			54	55.4	68	69.4
$\langle E \rangle$, kcal/mol			100	101	100	101
$k_{\rm a}({\rm exptl}), {\rm s}^{-1}$			3.9×10^{9}	8.7×10^{8}	4.9×10^{7}	1.1×10^{7}
$k_{\rm a}$ (calcd), s ⁻¹			4.0×10^{9}	1.9×10^{9}	4.5×10^{7}	1.9×10^{7}
$[k_a^{\rm H}/k_a^{\rm D}](\text{exptl})$			4.4 ± 0.9		4.4 ± 0.9	
$[k_a^{\text{H}}/k_a^{\text{D}}]$ (calcd)			2.1		2.4	

^a Hindered rotor treated as a torsion. ^b Partition function form for unit reaction path degeneracy at 800 K.

of 11 250 counts to the CFCl=CH₂ yield for each analysis gave a zero intercept. For CD₃CFCl₂*, the addition of 900 counts to the decomposition product's digital integrator counts would result in an intercept through the origin. These adjustments in the CFCl=CH₂ yield would cause an increase in both the rate for k_{HCl} and k_{DCl} of 32.8 and 31.3%, respectively, but would not change the kinetic isotope effect. Increasing the rates 30% would require E_0 's 1 kcal/mol lower than the recommended values.

The experimental rate constants from Figures 2 and 3 give the kinetic isotope effect, $k^{\rm H}/k^{\rm D} = 4.4 \pm 0.9$ for HCl/DCl; HF/ DF appears to be identical. Other chemically activated trisubstituted haloethanes with one primary and two secondary deuterium isotope effects gave $k^{\rm H}/k^{\rm D}$ slightly above 3,⁷ making the present system one of the largest $k^{\rm H}/k^{\rm D}$'s reported.

Attempts to replicate the large deuterium kinetic isotope effect required RRKM models with nearly complete fission of the C-H bond; a bond order near 0.1 has been recommended^{6,34} for chemically activated haloethanes. In addition, the ³⁷Cl/ ³⁵Cl thermal isotope effect³⁵ is very small, suggesting only moderate lengthening of the C-Cl bond and little Cl motion in the reaction coordinate. The MO calculation of Toto et al.9 furnishes bond orders between 0.36 and 0.7 for C-H and between 0.02 and 0.12 for C-X, and it is not clear that these would match the large experimental deuterium isotope effect and the small isotope effect for chlorine. Increasing numbers of α -halogens increase the k^{H}/k^{D} 's for chemically activated haloethanes,⁷ suggesting that the C-H bond weakens. By contrast, the MO calculations⁹ show a monotonic increase in the C-H bond order for HCl elimination: 0.512 (chloroethane) to 0.700 (1,1,1-trisubstituted ethanes) and the large bond order indicates little motion of H as the transition state forms. The C-H bond orders for the HF elimination transition states are calculated to be approximately 0.39, independent of α -halogenation. This suggests a much greater deuterium isotope effect for loss of HF versus HCl, but this has not been experimentally confirmed.

3. RRKM Calculated Unimolecular Rate Constants and Threshold Energies. Primary goals of this work are to determine threshold energies for elimination of HCl and HF from CFCl₂CH₃ and to compare these with E_0 's for other haloethanes in order to understand the effect of F and Cl substituents. The E_0 's were ascertained by constructing RRKM models and varying threshold energies until the calculated rate constants were in agreement with the experimental k_a 's. Arrhenius parameters have not been reported for thermal decom-

position of CFCl₂CH₃. To facilitate comparisons, the thermal preexponential factors for loss of HF and HCl and the RRKM models were developed using the same methodology employed in earlier work.⁷ Vibrational frequencies for CFCl₂CH₃ are known,²¹ and those for CFCl₂CD₃ were estimated from CFCl₂-CH₃ by comparing frequencies of CF₃CH₃ with CF₃CD₃.^{36,37} For the four-member transition state, the frequencies were assigned from previous models^{6,7,30} with the ring puckering adjusted to produce the desired preexponential factor; see Table 1. The reaction path degeneracies are based upon a torsional model.

The average energy, $\langle E \rangle$, of CFCl₂CH₃* is normally determined from the enthalpy of reaction 3b. We anticipate that $\langle E \rangle \approx 100$ kcal/mol based on the $\langle E \rangle$ for chemically activated CH₃CF₃ and CFCl₂CH₃.^{7,38,39} A value near 100 kcal/mol is in accord with a recent ab initio calculation⁴⁰ of the bond dissociation energies for a series of fluoroethanes in which the bond energies for CH_3CX_3 (X = halogen) are predicted to be 6 kcal/mol higher than for ethane because of the increased ionic character in the C-C bond. The enthalpy of formation at 298 K for CFCl₂CH₃ is not available; it was estimated as -83.1 kcal/mol from group additivity schemes,41 and adjustment to 0 K gave -82.6 kcal/mol. For the methyl radical $\Delta H_{\rm f}^{\circ}(0) = 35.9$ kcal/mol,⁴² and for the CFCl₂ radical a recent measurement⁴³ at 298 K of -22 ± 2 kcal/mol was corrected to -23.9 kcal/ mol at 0 K. ΔH°_{rxn} for reaction 3b at 0 K is -94.6 kcal/mol, and addition of 3.8 kcal/mol thermal energy for CFCl₂CH₃ and an $E_a = 1$ kcal/mol for radical combination give an estimated $\langle E \rangle = 99.4$ kcal/mol. Considering that the uncertainty in the experimental $\Delta H_{\rm f}^{\circ}$'s is at least ± 2 kcal/mol, we have selected 100 kcal/mol as the $\langle E \rangle$ for chemically activated CFCl₂CH₃. Using $\langle E \rangle = 100$ kcal/mol, the calculated rate constants match the experimental values with $E_0(\text{HCl}) = 54$ kcal/mol and $E_0(\text{HF}) = 68 \text{ kcal/mol.}$ Table 1 is a summary of the RRKM models, the rate constants, and the isotope effects.

4. Threshold Energies, Substituent Effects, and Transition State Atomic Charges. Toto *et al.*⁹ calculated the activation energies for CFCl₂CH₃, and because the E_0 's are normally 2 kcal/mol lower, we have reduced the computed E_a 's by that amount. For CFCl₂CH₃, this gives E_0 (HCl) = 56.4 kcal/ mol and E_0 (HF) = 63.9 kcal/mol, which are 2.4 higher and 4.1 kcal/mol lower, respectively, than our experimental numbers. This agreement would be considered satisfactory because the experimental uncertainty is ± 2 kcal/mol. However, a more compelling comparison is the difference in the E_0 's, because, for both the experiment and the calculations, relative results are more reliable than absolute values. The calculated difference in the two threshold energies is 7.5 kcal/mol, which is about half the experimental result of 14 kcal/mol and is clearly outside the experimental uncertainty unless there exists a very large undetected experimental error. For HF elimination, replacing H's with F's results in an increase in the threshold energies from CH₂FCH₃ (58 kcal/mol) to CHF₂CH₃ (61 kcal/mol) to CF₃-CH₃ (68 kcal/mol). Replacing H's with Cl substituents has the same effect upon the E_0 (HF) as replacement of H's with F's; E_0 's for CF₃CH₃, CF₂ClCH₃, an CFCl₂CH₃ are, within the experimental error, identical at 68, 69.5, and 68 kcal/mol, respectively. Therefore, for HF elimination, Cl and F substituents are equivalent; they increase E_0 .

For HCl elimination from both mono- and dichlorinated haloethanes, replacing an H with an F does not appreciably alter the threshold energies. The E_0 (HCl)'s for CH₂ClCH₃ and CF₂-ClCH₃ are identical at 55 kcal/mol and are 52 and 54 kcal/mol for CHCl₂CH₃ and CFCl₂CH₃, respectively. The small decline in E_0 with additional chlorines could arise from steric considerations. Steric crowding present in the molecule would be reduced with elongation of the C–Cl bond so that successive chlorine substitution would raise the energy for the reactant more than for the transition state, thereby reducing E_0 . When HF is eliminated, the steric repulsions involving the Cl substituents in the molecule and the transition state structures are the same so there is no effect on the threshold energy.

It appears that Cl or F substituents raise the barrier for loss of HF about 3-7 kcal/mol per halogen substituent; however, F substituents have little effect on the barrier for loss of HCl. There are at least two possible explanations for these observations: (1) Halogen substituents have the ability to release or remove electron density from their neighbor; fluorine is both a stronger σ acceptor and π donor than chlorine. A complex interplay of these two tendencies could be responsible for the observed trends when multiple halogens are present so that analysis of substituent effects on the threshold energies is not straightforward. If this is the case, much more experimental and theoretical work will be needed to unravel the intricacies of halogen substitution. (2) Halogen substituents exert similar inductive effects, and the HCl and HF transition states differ.⁷ Opposing trends in the E_0 's could result from an α -carbon that has little additional charge development for HCl elimination but significant change in the charge density when HF is removed. If there is minimal change in the charge on the α -carbon for HCl elimination, then the nature of the substituent would not influence E_0 and H, F, and Cl substituents would have similar threshold energies. This is exactly the observed trend in the E_0 's if Cl's steric size accounts for the decline in E_0 with successive Cl substitution. We cannot determine whether the α -carbon develops a more positive or more negative charge as the transition state forms because it is unclear if halogen substituents donate or remove electron density.

In analyzing substituent effects, it is essential that the *change* in the electron density as the reactant forms the transition state be considered. A carbon with a large atomic charge that maintains the same charge in the transition state will not experience any variation in E_0 with substitution of halogen for hydrogen, as the effect on the transition state is countered by a corresponding change in the stability of the reactant. Several conclusions of Toto *et al.*⁹ differ from ours; it appears that they considered only the absolute and not the evolution of the atomic charges.

The atomic charges computed⁹ for all possible chloro-/fluorosubstituted ethanes will now be analyzed to determine if the calculations support the proposal that the two transition states



Figure 4. Change in the calculated atomic charges for the HCl and HF elimination transition states for $CFCl_2CH_3$ from Table 15 in ref 9. The absolute charges on each atom of the reactant molecule are given in the text.

have different charge characteristics. According to the calculations,⁹ the α -carbon is becoming more positively charged when HCl is lost (the transition states' α -carbons are 0.24 \pm 0.04 more *positive* than in the reactant) but less positively charged when HF is lost (the transition states' α -carbons are 0.11 \pm 0.05 more *negative* than in the reactant). Hiberty¹² calculated atomic charges for chloroethane very close to those of Toto *et al.*⁹ To be consistent with our trends in the *E*₀'s when H is replaced by Cl and/or F, both halogen substituents would need to be very slightly electron donating (almost inductively neutral) when HCl is lost, but both Cl and F must be more strongly electron donating when HF is eliminated. Figure 4 shows the change in the atomic charges calculated for each atom of CFCl₂-CH₃ when HCl and HF are removed.

The charges calculated for the CFCl₂CH₃ reactant are negative on the F substituent (-0.26) with the two Cl's being almost neutral (-0.02). The α -carbon holds a partial positive charge (+0.16) due to these electron withdrawing substituents. As the transition state forms, electrons flow to the halogen being lost and it develops a greater negative charge. In turn, all α -substituents become more positive as they feed electron density to the α -carbon; the Cl substituents actually develop a greater positive charge, and the F becomes less negative (see Figure 4). These changes on the leaving atom and on the substituents occur irrespective of the identity of the halogen being eliminated. However, the change in the α -carbons's charge does depend upon the halogen being lost. For HCl, the α -carbon becomes more positive as the departing Cl removes electron density in preparation for leaving with the hydrogen. For HF elimination, the α -carbon accepts electron density from the substituents and becomes negatively charged. This analysis obviously indicates different transition states and would result in opposing trends in the E_0 's for substituents that donate electron density. For loss of HF, the F and Cl substituents would intensify the developing negative charge on the α -carbon and raise the E_0 's. By contrast, for loss of HCl, the donation of electron density would stabilize the α -carbon's additional positive charge and decrease the threshold energy.

Although the calculated charges⁹ are consistent with the trends observed for CFCl₂CH₃ and CF₂ClCH₃, the magnitude appears too large when HCl is removed. At the α -carbon the change in the charge is greater for HCl versus HF elimination, suggesting that Cl and F substituents would have a greater influence on the E_0 (HCl) than E_0 (HF), counter to experimental observations. Perhaps further refinement of the calculations would improve agreement.

The movement of electrons just described is reminiscent of models that involve three pairs of electrons.^{5,12} The electron pair of the C–X bond shifts toward the departing halogen, increasing its negative charge. A lone pair on the halogen shifts

toward the hydrogen as the H–X bond forms and the bond pair of the C–H bond moves to become the π -bond between the carbons.

We also note that the calculations⁹ suggest that there is almost no change in electron density at the β -carbon when HCl is lost, but the β -carbon becomes slightly more negatively charged at the transition state for HF elimination. This suggests that β -substituents will not alter E_0 (HCl). By contrast, electron withdrawing substituents at the β -carbon will increase and electron donating substituents will decrease E_0 (HF).

Assuming that these calculated atomic charges for the α -carbon are of the correct sign, the models require both Cl and F to provide electron density to the α -carbon. Comparing the observed effects of the Cl and F substituents with CF₃, a known electron withdrawer, or CH₃, capable only of providing electron density, the sign on the α -carbon can be confirmed. Experiments are in progress in our laboratory to provide threshold energies for systems with α -CF₃ or CH₃ substituents, and we will begin determining E_0 's for 1,2-dehydrohalogenations involving β -carbon substituents.

Conclusions

Unimolecular rate constants measured for the unimolecular 1,2-dehydrohalogenation of chemically activated CFCl₂CH₃ gave threshold energies indicating that fluorine and hydrogen substituents are comparable for HCl elimination; fluorine's electronic effects are minimal, and E_0 is only slightly affected. For HF elimination, Cl substituents behave the same as F; they raise E_0 by 3–7 kcal/mol per halogen. A possible explanation, contrary to the traditional view,^{3,4,6,8} is that the transition states for 1,2-dehydrochlorination and 1,2-dehydrofluorination develop partial charges at the α -carbon, the carbon containing the departing halogen, that have different signs, and the Cl and F substituents exert similar inductive effects; both either provide or withdraw electron density from the α -carbon. The absolute sign of the partial charge on the α -carbon cannot be determined due to the 2-fold nature of halogen substituents; they are both π donors and σ acceptors of electron density. Recent *ab initio* calculations⁹ support dissimilar transition states for loss of HF and HCl; assuming they furnish the correct sign for the partial charge developing on the α -carbon, the Cl and F substituents are electron donors. However, experimental confirmation for the sign of the charge emerging as the reactant is converted to products would be beneficial.

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