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Threshold Energies and Substituent Effects for Unimolecular Elimination of HCl (DCl) and HF (DF) from Chemically Activated CF_2ClCH_3 and CF_2ClCD_3

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Chemically activated CF_2ClCH_3-d_0 and -d_3 were prepared with 101 and 102 kcal/mol of internal energy, respectively, by the combination of CF_2Cl with methyl-d_0 and -d_3 radicals at 300 K. The CF_2ClCH_3 reacts by loss of HCl and HF with rate constants of $(2.5 \pm 0.4) \times 10^9$ and $(0.10 \pm 0.02) \times 10^9$ s^{-1}, respectively, a branching ratio of 25:1 in favor of HCl. The CF_2ClCD_3 has rate constants of $(0.78 \pm 0.12) \times 10^9$ for loss of DCl and $0.033 \pm 0.005 \times 10^9$ sec^{-1} for loss of DF. The combined primary and secondary isotope effect was 3.2 ± 0.9 for HCl/DCl elimination and 3.0 ± 0.9 for loss of HF/DF. RRKM theory was used to model these unimolecular rate constants to determine the threshold energy barriers, E_0's, for the four-centered elimination reactions. The E_0's were 55 ± 2 kcal/mol for dehydrochlorination and 69.5 ± 2 kcal/mol for dehydrofluorination. These threshold barriers are in sharp disagreement with prediction based on trends in the E_0's for a series of mono-, di-, and trisubstituted chloroethanes and a similar series of fluoroethanes. An analysis of the E_0's for the chloroethanes, fluoroethanes, and chlorodifluoroethane suggests that the carbon-halogen bond in the transition state changes from a nearly neutral C-Cl bond for HCl loss to a C-F bond that has much greater charge separation when HF is eliminated.

Introduction

Common methods of providing a unimolecular reactant with vibrational and rotational energy in excess of the minimum barrier that leads to product formation include thermal heating,[1] chemical activation,[2,3] and photolytic excitation. On the ground-state electronic energy surface, photolysis could be accomplished by infrared multiple photon decomposition (IRMPD)[4,5] or absorption of a UV photon[6-9] corresponding to one or more quanta in a specific mode.

For a unimolecular reactant with multiple reaction paths the branching ratio will normally be only slightly dependent on the energy[3] and thus on the activation process, unless the Arrhenius *A* factors are significantly different. If the distribution of the excitation energy among the vibrational modes is rapid compared to the rate of reaction and if the transition states are well characterized, then RRKM theory can be fitted to the observed branching ratios to accurately determine the difference in the threshold energies, E_0. For cases where the experimental rate constants are also known, the absolute value of the E_0's can be assigned to within ± 2 kcal/mol.

Measuring a series of reaction rates for a specific reaction type, in which substituents are altered in an orderly manner, provides trends in E_0's that can aid in the understanding of inductive or resonance effects that influence the activation energies. For loss of HF from fluoroethanes or the elimination of HCl from chloroethanes, the trends in E_0's are well established for successive replacement of an H by a halogen.[3,10,11] It appears that increased chlorine substitution on the carbon containing the halogen (the α-carbon) decreases the threshold energy (CH_3CH_2Cl, 55; CH_3CHCl_2, 52; CH_3CCl_3, 50 kcal/mol). By contrast, the critical energy for HF elimination increases with F substitution at the α-carbon (CH_3CH_2F, 58; CH_3CHF_2, 61; CH_3CF_3, 68 kcal/mol). For mixed halogenated species, however, the trend has not been carefully investigated, so that the effects of Cl substituents on the HF barrier, E_0(HF), or fluorine substituents on the HCl threshold energy, E_0(HCl), are uncertain.

The nature of the four-centered transition state has been extensively discussed,[2,3,10] and only the salient features will be summarized here. Substituent effects have been rationalized by assuming an ionic transition state with a partial positive charge on the α-carbon and a partial negative charge on the β-carbon.[12] Different trends in the E_0's for chlorine and fluorine substituents at the α-carbon have been attributed[3,12] to fluorine's electron-withdrawing (inductive) effect, which destabilizes the developing positive charge. A resonance effect that delocalizes an electron lone pair on the chlorine into the π-bond emerging between the two carbons would stabilize the partial positive charge on the α-carbon and lower the E_0.

The present study involves 1,1,1-chlorodifluoroethane, which was chemically activated by combination of methyl and difluorochloromethyl radicals. Photolysis of methyl iodide and difluorochloroacetic anhydride was used to generate the CH_3 and CF_2Cl radicals, respectively. Competing four-centered unimolecular elimination pathways for CH_3CF_2Cl include dehydrochlorination and dehydrofluorination. If the trends that were previously discussed for the series of chloro- and fluoroethanes are additive for haloethanes containing both Cl and F, then the HF barrier can be estimated as slightly below 60 kcal/mol and the threshold energy for HCl loss should be near 65 kcal/mol. The HF barrier was estimated by starting with CH_3CHF_2 (61 kcal/mol) and lowering the value a few kcal/mol for replacement of the H by a chlorine. The HCl barrier was determined by increasing the barrier for CH_3CH_2Cl (55 kcal/mol) about 10 kcal/mol for substitution of two fluorines for the hydrogens. Selection of CF_2ClCH_3 for this study was based on the expectation that the rates should be competitive, with HF elimination being slightly faster than loss of HCl.

Although CF_2ClCH_3 has been previously investigated, there is disagreement among the studies. Data from pyrolysis suggest that dehydrochlorination is favored. At the highest temperatures employed, one study,[13] found a branching ratio (HCl:HF) of 2.3:1, but three other studies[6,14,15] placed it much higher, near 10:1. At

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lower temperatures the ratio increased to almost 100:1. Also, the IRMPD studies are in disagreement. Only HCl elimination is found in two cases,[16,17] but in another[18] the branching ratio was 2:1. The only previous chemical activation study[19] was published in 1968 and reported a branching ratio of 1:4 in favor of HF elimination. The preceding analysis of the trends in the E_0's predicting that HF is the dominant process, in general, disagrees with these observations.

Because there is considerable discrepancy among the previous studies, we investigated the deuteriated analogue, CF_2ClCD_3, to provide additional experimental evidence for the branching ratio. The data also permit comparison of the isotope effect for CF_2ClCH_3/CF_2ClCD_3 with other chemical activated chloro- and fluoroethanes. These isotope effects furnish another check on the reliability of the chemical activation rate constants. The primary goals of this study are to measure the branching ratio and to use RRKM theory to determine the threshold energies, and thus the substituent effects, for four-centered HX elimination from mixed haloethanes.

Experimental Section

A total of 2 cm^3 (STP) of methyl iodide and difluorochloroacetic anhydride was measured with a Datametrics 1400 electronic manometer and placed in quartz vessels ranging in volume from 67 to 240 cm^3. The vessels contained about 0.5 g of Hg_2I_2. The mercury(I) iodide assisted production of methyl radicals by removal of iodide atoms.[20] Pressures exceeding the vapor pressure of the reactants were achieved with a bath gas of SF_6, and the typical compositions were sulfur hexafluoride = 84.2 μmol, methyl iodide = 3.4 μmol, and difluorochloroacetic anhydride = 1.6 μmol; this corresponds to reactant ratios of 50:2:1. The mixture was photolyzed at room temperature for 10 min by using an unfiltered Oriel 200-W high-pressure mercury lamp. These conditions typically achieved 15% methyl iodide conversion. The products of the reaction were analyzed on a Perkin-Elmer 3920 gas chromatograph (FID) with a combination column of 20-ft Porapak R and 14-ft Porapak T.

Identification of the reaction products was based on comparison of GC retention times with known compounds. Mass spectral and infrared analyses were done to confirm assignment for $CF_2{=}CH_2$, CF_2ClCH_3, and CF_2ClCF_2Cl. Yields of the other products were too small for IR or MS confirmation, so their identity was based only on their GC retention time and the expected pressure dependence of their yield. All the compounds were purchased from PCR except for methyl iodide-d_0 and -d_3 and methyl chloride, which were obtained from Aldrich. The order of elution and typical retention times were as follows: $CF_2{=}CF_2$ (32.6 min), C_2H_6 (33.2 min), $CF_2{=}CH_2$ (37.5 min), CF_2Cl_2 (60.9 min), CH_3Cl (63.0 min), $CFCl{=}CH_2$ (64.5 min), CF_2ClCH_3 (70.7 min), CF_2ClCF_2Cl (73.5 min), and CH_3I (106 min). The ethane was not separated from $CF_2{=}CF_2$, so these could not be quantified. The separation was not complete between CF_2Cl_2, CH_3Cl, and $CFCl{=}CH_2$; the height of the valley between the peaks was typically 20–40% of the peak height, and there was also a slight overlap of the $CFCl{=}CH_2$ and CF_2ClCH_3; the valley between the peaks normally was less than 5% of the peak height. Although SF_6 does not burn, it broadens and distorts the first three peaks in the GC analysis if the entire mixture is used. Resolution of the three peaks is destroyed unless the sample size is reduced. Therefore, just 5–30% of a photolysis sample, equilibrated for at least an hour, was analyzed each time. At least two analyses were obtained for each sample. A Shimadzu C-R5A chromatopac recording integrator acquired data and integrated the GC peak areas.

TABLE I: Response Factors for the FID Gas Chromatograph Relative to CF_2ClCH_3

molecule[a]	response	molecule	response
C_2H_6	1.02 ± 0.05	$CH_2{=}CFCl$	1.04 ± 0.06
CH_3Cl	8 ± 1	CF_2Cl_2	4.38 ± 0.17
$CH_2{=}CF_2$	1.07 ± 0.05	CF_2ClCF_2Cl	2.00 ± 0.03

[a] Based on 12 calibration mixtures with multiple runs (between 6 and 12) of each mixture.

Calibration mixtures, containing known compounds, were analyzed under the same conditions as the reaction mixture, and the response factors are listed on Table I. The response factors for the deuteriated products were assumed to be the same as for the nondeuteriated analogues. Twelve separate calibration mixtures with multiple runs per sample were analyzed. A consistent response factor for CH_3Cl was difficult to obtain even within a single mixture, and the CH_3Cl response factor increased with increasing equilibration time. The reason may be either that fractionation occurred during equilibration or that CH_3Cl was somehow absorbed in the GC inlet system or in the O-rings of the stopcocks. Fractionation was not believed to occur because consistent response factors were obtained for the other compounds, even after an overnight equilibration period. Although the response factor for CH_3Cl is higher than expected, the averaged value was used because the treatment of the calibration runs closely replicated the method employed with photolyzed samples.

Experimental Results

The chemically activated CF_2ClCH_3 was formed by combination of CH_3 and CF_2Cl radicals. The mechanisms of the formation of the desired radicals from CH_3I and $(CF_2ClCO)_2O$ are presented elsewhere[20,21] and will not be discussed here. The mechanism given in reactions 1–6 accounts for the formation of

$$\cdot CF_2Cl + \cdot CH_3 \xrightarrow{k_d} CH_3Cl + :CF_2 \tag{1a}$$

$$\cdot CF_2Cl + \cdot CH_3 \xrightarrow{k_c} CF_2ClCH_3^* \tag{1b}$$

$$CF_2ClCH_3^* \xrightarrow{k_{HCl}} CF_2{=}CH_2 + HCl \tag{2}$$

$$\xrightarrow{k_{HF}} CFCl{=}CH_2 + HF \tag{3}$$

$$\xrightarrow{k_M[M]} CF_2ClCH_3 \tag{4}$$

$$\cdot CF_2Cl + \cdot CF_2Cl \xrightarrow{k_d} CF_2Cl_2 + :CF_2 \tag{5a}$$

$$\cdot CF_2Cl + \cdot CF_2Cl \xrightarrow{k_c} CF_2ClCF_2Cl \tag{5b}$$

$$\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3 \tag{6}$$

the products observed (k_d and k_c represent the rate constants for disproportionation and combination, respectively). The CH_3CH_3 and CF_2ClCF_2Cl are stable at the pressures of our experiment. All stable products were observed and those for reactions 2–4 were measured as a function of pressure. The difluorocarbene is believed to dimerize[22,23] to give $CF_2{=}CF_2$. In this system the carbene might also combine with either methyl or difluorochloromethyl radicals, reactions 7 and 8, or abstract iodine from

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the methyl iodide to form additional iodination products.

$$:CF_2 + {}^{\bullet}CF_2Cl \rightarrow {}^{\bullet}CF_2CF_2Cl^* \tag{7}$$

$$:CF_2 + {}^{\bullet}CH_3 \rightarrow {}^{\bullet}CF_2CH_3^* \tag{8}$$

The haloethyl radicals from reactions 7 and 8 are chemically activated, and if they form they might decompose to give Cl atoms and tetrafluoroethene in the case of $^{\bullet}CF_2CF_2Cl^*$ or $CF_2{=}CH_2$ and H in the case of $^{\bullet}CF_2CH_3^*$. The tetrafluoroethene presents no complications, but the 1,1-difluoroethene is also formed from $CH_3CF_2Cl^*$ via reaction 2. Because the yield of $CF_2{=}CH_2$ is needed to determine the rate for HCl elimination, an additional source would invalidate the rate constants unless a constant fraction of $CF_2{=}CH_2$ was formed. The rate for H ejection from $^{\bullet}CF_2CH_3^*$ has been calculated[24] by RRKM theory as 10^{12} s^{-1}, indicating that all the $^{\bullet}CF_2CH_3^*$ would react to form $CF_2{=}CH_2$ under our experimental conditions. Data presented later will show that no additional $CF_2{=}CH_2$ is formed, and thus reaction 8 is not important in our system.

It is often useful to compare the calculated cross-combination ratio, $X_c = \sum k_{1-4}/(\sum k_5 \sum k_6)^{1/2}$ to the experimental results. From collision theory, the predicted value for the interaction of two hard-sphere radicals is $X_c = 2$. However, Pritchard and coworkers[25] have shown that values different than 2 are obtained when the distinct masses and collision cross sections of the radicals are considered. Regardless, the calculated and experimental values of X_c should be similar if the assumed mechanism is correct. The model developed by Pritchard and co-workers[26] was used to determine an experimental cross-combination ratio of 2.2 ± 0.2. A theoretical value of 2.4 was calculated from the expression used by Arthur and Christie.[27] The large scatter in our number is attributed to the difficulty in measuring the areas of CH_3Cl and CF_2Cl_2 and problems of accounting for both the decomposition products from reactions 2 and 3 and the disproportionation products from reactions 1a and 5a.

Our disproportionation/combination ratio, $k_d/k_c = k_{5a}/k_{5b}$, can be compared with previous measurements for CF_2Cl radicals. In a study of the product quantum yields from the photolysis of $(CF_2ClCO)_2O$, Watkins and Whittle[21] determined the k_d/k_c for CF_2Cl radicals to be 0.13 at 295 K and 0.21 at 474 K. These results were based on seven and five experimental trials, respectively. Majer and co-workers[28] reported k_d/k_c as 0.09 at 486 K and 0.20 at 541 K on the basis of six and five trials, respectively. Prichard and Perona[29] found $k_d/k_c = 0.17 \pm 0.038$ on the basis of 20 trials at 298 K and 2 trials at 396 K gave 0.42 and 0.30. We find a k_d/k_c ratio for CF_2Cl radicals, based on 50 trials, of 0.17 ± 0.05 at ambient temperature. The experimental uncertainty mainly results from the difficulty of measuring the area of the CF_2Cl_2 peak. Our k_d/k_c determination is between the values found by Watkins and Whittle and by Majer and is the same as Prichard and Perona's. Because Prichard's study and this work are more extensive, we recommend 0.17 for k_{5a}/k_{5b}. The larger values at higher temperatures suggests that abstraction of Cl from the radical precursor produces additional CF_2Cl_2 or that the disproportionation reaction is aided at higher temperatures because fission of the C–Cl bond is easier. The similarity between the theoretical and experimental X_c and the reasonableness of our k_d/k_c for CF_2Cl radicals gives us confidence in the reaction scheme (1)–(6) and in our experimental methodology.

For CH_3 and CF_2Cl radicals the $k_d/k_c = k_{1a}/k_{1b}$ can be determined from the $[CH_3Cl]/([CF_2ClCH_3 + CF_2{=}CH_2 + CFCl{=}CH_2])$. Our value of 0.24 ± 0.05 (48 trials) should be considered tentative because of the uncertainty associated with adding the yields of the decomposition and stabilized products and the difficulty of obtaining a consistent FID calibration factor for the methyl chloride.

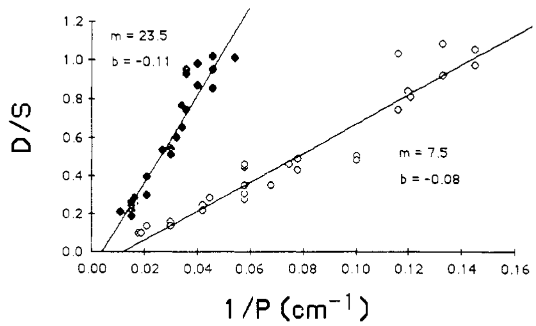

Figure 1. $[CF_2{=}CH_2]/[CF_2ClCH_3]$ versus reciprocal pressure plot for chemically activated CF_2ClCH_3-d_0 (filled symbols) and -d_3 (open symbols).

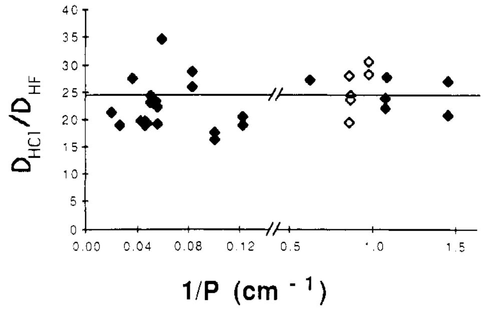

Figure 2. $[CF_2{=}CH_2]/[CFCl{=}CH_2]$ versus reciprocal pressure plot for chemically activated CF_2ClCH_3-d_0 (filled symbols) and -d_3 (open symbols).

The activated CF_2ClCH_3 molecules, containing 101 kcal/mol of internal energy (see the Appendix for the thermochemistry), may eliminate HCl or HF or be stabilized by collision. In the strong collision limit, the chemical activation rate constants can be calculated from[3]

$$k_{ai} = k_M[M](D_i/S_i)$$

where $k_M[M]$ is the collision frequency and D_i and S_i denote measured yields of the decomposed and stabilized products, respectively. Figure 1 is the plot of D/S vs $1/P$ for HCl and DCl elimination. The plot shows only the linear portion corresponding to $D/S < 1$. Beyond this point, the plot exhibits the usual upward curvature indicating cascade deactivation. A weighted average of the collision diameters (5.9 Å, (SF_6), 5.0 Å (CH_3I), 8.0 Å (anhydride), and 5.4 Å (CF_2ClCH_3 and CF_2ClCD_3)) was used to calculate k_M. The collision diameters for methyl iodide and sulfur hexafluoride are known,[30] and those for the anhydride and haloethane were estimated by comparisons with similar molecules.[30] Because the temperature dependence for the collision diameters, $\Omega^{2,2}$ integrals, are not known for these molecules, inclusion of a temperature-dependent factor is not warranted. The rate constants obtained for HCl and DCl elimination were (2.5 ± 0.4) × 10^9 and (0.78 ± 0.12) × 10^9 s^{-1}, respectively. For HF and DF eliminations, the rate constants were determined from a plot of D_{HCl}/D_{HF} versus the reciprocal pressure (Figure 2). Dehydrofluorination was found to be 25 ± 4 times slower than the corresponding dehydrochlorination process, giving rate constants of (0.10 ± 0.02) × 10^9 and (0.033 ± 0.005) × 10^9 s^{-1} for HF and DF loss, respectively. There is more than the desired scatter in the data shown in Figures 1 and 2. For Figure 2, the uncertainty is mainly from the difficulty with measuring the very small yield of $CFCl{=}CH_2$, which is not completely resolved from CH_3Cl. The negative intercept for both the D/S plots in Figure 1 may be caused by a removal of 1,1-difluoroethane by a secondary reaction, additional CF_2ClCH_3 formed by a reaction other than (1b), an incorrectly calibrated electronic manometer giving

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TABLE II: Summary of Experimental Rate Constants and RRKM Models for 1,1,1-Difluorochloroethane

	molecules		activated complexes, elimination of			
	CF_2ClCH_3	CF_2ClCD_3	HCl	DCl	HF	DF
vibr freq and degeneracies, cm^{-1}	3002 (3)	2246 (3)	3025 (2)	2284 (2)	3025 (2)	2284 (2)
	1297 (6)	1122 (5)	1446 (1)	1138 (5)	1411 (4)	1452 (3)
	930 (2)	770 (4)	1160 (4)	798 (2)	1110 (1)	1083 (2)
	679 (1)	480 (2)	920 (4)	597 (2)	902 (4)	798 (2)
	498 (3)	432 (1)	546 (3)	480 (2)	523 (3)	580 (1)
	322 (2)	310 (2)	500 (1)	390 (3)	432 (1)	455 (4)
	238 (1)[a]	160 (1)	375 (2)	350 (1)	331 (2)	315 (3)
moments of inertia $I_x/I_y/I_z$, amu Å^2	153.5	159.0	155.4	161.5	155.1	166.6
	90.6	101.6	88.5	97.9	149.6	161.3
	161.7	175.0	150.8	163.2	92.2	103.9
reaction path degeneracy			2	2	4	4
preexponential factor,[b] s^{-1}			7.1×10^{12}	7.9×10^{12}	9.0×10^{12}	12.0×10^{12}
E_0, kcal/mol			55	56.4	69.5	71.0
$\langle E \rangle$, kcal/mol			101	102	101	102
k_a(exptl),[c] s^{-1}			$(2.5 \pm 0.4) \times 10^9$	$(0.78 \pm 0.12) \times 10^9$	$(0.10 \pm 0.02) \times 10^9$	$(0.033 \pm 0.005) \times 10^9$
k_a(calcd), s^{-1}			2.2×10^9	1.0×10^9	0.088×10^9	0.040×10^9
$[k_a{}^H/k_A{}^D]$(exptl)[d]			3.2 ± 0.9		3.0 ± 0.9	
$[k_a{}^H/k_a{}^D]$(calcd)			2.2		2.2	

[a] Hindered rotor treated as a torsion. [b] Partition function form for unit reaction path degeneracy at 800 K. [c] Uncertainity based on 15% error. [d] Compounding errors from the uncertainity in the experimental rate constants accounts for the large deviation.

pressure readings that are too large, or the negative intercept may just reflect the experimental uncertainty in the data. The process most likely to reduce the yield of alkene would be addition of CF_2Cl radicals to the alkene. We did photolyze difluorochloroacetic anhydride and $CF_2{=}CH_2$ using conditions mimicking our *D/S* study and found that the reaction was too slow to be important and that the major products from the addition of CF_2Cl radicals to the C=C were not observed in our kinetic study. We are unable to propose logical reactions that would produce excess CF_2ClCH_3. Because the intercepts are similar in the undeuteriated and deuteriated study, we conclude that an error in the calibration of the manometer is probably responsible for the nonzero intercept. A zero or slightly negative intercept supports our earlier conclusion that reaction 8 is not important because additional $CF_2{=}CH_2$ would result in a positive intercept for Figure 1. In any case, the rate constants were determined from the slopes of the data in Figure 1, so shifting the data toward the right or left as a result of either removal of difluoroethene or a pressure error would have little effect on the rate constant.

Discussion

Comparison of the Branching Ratio for CH_3CF_2Cl with Previous Studies. In seasoned vessels, thermal activation experiments[6,13–15] find that loss of HCl is dominant, and the branching ratio is greater than 100:1 at temperatures below 700 K. At higher temperatures loss of HF is observed, and at 770 K the branching ratio is about 10:1. For one study[13] the branching ratio at 770 K was 2.3:1, which seems too large compared to other thermal activation results. Dong et al.[6] recently analyzed all the thermal data and recommended an *A* factor of 9.8×10^{12} s^{-1} and an activation energy of 55.6 ± 2 kcal/mol for HCl elimination. Arrhenius parameters for loss of HF could not be recommended because the yield was too low and the data were not reproducible. Our RRKM model, that will be presented later, agrees with the recommended Arrhenius parameters.

Four groups[4,16–18] have reported IRMPD of CF_2ClCH_3. All find that loss of HCl has the lowest E_0, but the reported branching ratio varies considerably. Lee and co-workers[16] and Zitter and co-workers[17] report just elimination of HCl. Sondag and Wegdam[4] find loss of HF only at the highest power levels, but West et al.[18] report a branching ratio of 2:1 and that the threshold for elimination of HCl is only slightly lower than the barrier for loss of HF. However, Flynn and co-workers[18] measured only the IR emission from HF and HCl and not the yield of the alkene product. Relating IR emission intensity to product ratios is not trivial because the analysis must properly account for the detector efficiencies, the Einstein *A* coefficients, and the vibrational relaxation rates for each hydrogen halide. West et al.[18] suggest that HF may be formed by subsequent IRMPD of the $CH_2{=}CF_2$ formed by loss of HCl from the parent molecule. Our experiments agree with those reporting mainly loss of HCl; therefore we conclude either that difficulties in the analysis of the IR emission resulted in an incorrect branching ratio or that the HF observed by West et al.[18] is produced via secondary reactions rather than direct excitation of CF_2ClCH_3.

The previous chemical activation study is the only investigation favoring a lower threshold for loss of HF, and that work was based on the product yield ratio of $CH_2{=}CFCl/CH_2{=}CF_2$. However, Phillips and Trotman-Dickenson[19] were unable to verify the identity of the alkene, $CH_2{=}CFCl$, formed by loss of HF. They observed one peak on the gas chromatogram that had a retention time close to the expected time for $CH_2{=}CFCl$ and assigned that to $CH_2{=}CFCl$. Phillips and Trotman-Dickenson used acetone to produce the methyl radicals. In the early stages of our work we attempted to use acetone as the methyl radicals source and found a significant, unidentified product with a retention time similar to $CH_2{=}CFCl$. This unknown is probably a carbonyl compound, but we did not attempt positive identification; rather we utilized CH_3I to produce methyl radicals. We believe that this unknown product was incorrectly identified as $CH_2{=}CFCl$, and thus the branching ratio reported by Phillips and Trotman-Dickenson is incorrect. We also note that even with our elaborate separation method, two products, CH_3Cl and CF_2Cl_2, were eluted very close to $CH_2{=}CFCl$.

RRKM Model. The unimolecular rate constants for CF_2ClCH_3 and CF_2ClCD_3 were calculated in the usual manner using the harmonic oscillator RRKM formulation and the Harrhoff approximation.[3] The principal objective is to assign reliable threshold barriers to the channels for elimination of HCl and HF. To maintain consistency with prior calculational methodologies, the four-centered HX elimination transition-state model, which has been applied satisfactorily to many haloalkanes,[2,10,31] was used. In that model bond orders assigned for the four-membered ring were 1.5 (C–C), 0.9 (C–Cl or C–F), 0.1 (H–Cl or H–F), and 0.1 (C–H or C–D), and the bond lengths were calculated by using Pauli's rule. The vibrational frequencies,[32] bond angles and lengths,[33] and moments of inertia[33] for CF_2ClCH_3 are known, and those for CF_2ClCD_3 were calculated or estimated by analogy with the molecular parameters for CF_3CH_3 and CF_3CD_3.[34,35] Moments of inertia for the complexes were then computed by using these bond angles and lengths and the above bond orders. For

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the complex, the vibrational frequencies of the four-membered ring involving HF and HCl loss were estimated from the transition-state frequencies for CF_2HCH_3[36] and $CH_2ClCHCl_2$.[10] The ring puckering and torsional frequencies were varied to match the desired preexponential factor, vide ante. The frequencies assigned to all deuteriated species fit the Teller–Redlich product rule to within 12%. Table II contains the parameters used for the molecular and activated complex models and a summary of the calculated and experimental rate constants. Calculated and experimental kinetic isotope effects are also shown in Table II. The threshold barriers (E_0's) that gave the best fit between the calculated and experimental rate constants are also included in Table II. These E_0's will be related to the substituent effects after the isotope effects are discussed.

Kinetic Isotope Effect. At room temperature the experimental intermolecular isotope effect for chemically activated CF_2ClCH_3/CF_2ClCD_3 was 3.2 ± 0.9 for loss of HCl/DCl and 3.0 ± 0.9 for loss of HF/DF. These values are close to those reported for chemically activated CF_3CH_3/CF_3CD_3, 3.1[37] at 470 K, 2.91[38] at 333 K, and 2.86[38] at 468 K. Since there appears to be little temperature dependence in the CF_3CH_3/CF_3CD_3 isotope effect, the close agreement with our room-temperature value is gratifying. Other chemically activated haloethanes with one primary and two secondary deuterium effects have slightly lower k^H/k^D than we found for CF_2ClCH_3/CF_2ClCD_3, CF_2HCH_3/CF_2HCD_3 (2.7),[36] CH_2FCH_3/CH_2FCD_3 (2.3),[36,39] and CH_2ClCH_3/CH_2ClCD_3 (2.2).[40] The general reduction in the k^H/k^D from approximately 3.1 to 2.7 to 2.3 parallels the decline in the number of halogen substituents on the α-carbon from 3 to 2 to 1. Error limits were not reported for most of these studies,[36–40] but the experimental uncertainty is normally ±20%. Thus, the variation in the isotope effect is probably within the combined experimental errors. There is no reason for the isotope effect to change with the number of halogen substituents unless the increased number of halogens alters the C–H or H–X bond order in the transition state. There is some justification for a differing extent of C–H bond rupture in the transition state. An increase in the number of halogen substituents on the α-carbon alters the C–H bond dissociation energy (BDE) at the β-carbon, e.g., the BDE increases 6.7 kcal/mol from ethane (100 kcal/mol) to CF_3CH_3 (106.7 kcal/mol).[41] For the series CH_2FCH_3, CF_2HCH_3, and CF_3CH_3 the range in the C–H bond dissociation energy of the CH_3 group might be greater than 6.7 kcal/mol because the C–H BDE for the fluoro-substituted methanes drops when the first F is added to methane and then increases; CH_4 (105.1), CH_3F (101.3), CF_2H_2 (103.2), CF_3H (106.7 kcal/mol).[41,42] An increase in the k^H/k^D as the number of halogen substituents increases is certainly conjecture at this point, and further experimental and theoretical work is necessary to determine if this trend is real or just a reflection of the experimental uncertainty.

The calculated $k^H/k^D = 2.2$ (Table II) agrees with previous calculated results and suggests that our measured values are too large or that a better model is needed. Our RRKM model was patterned after previous work to facilitate comparison of threshold energies; therefore, a k^H/k^D similar to previous calculations is expected. We did not attempt to improve the kinetic isotope calculations because our principle goal was to determine threshold energies.

α-Carbon Substituent Effects on E_0(HCl) and E_0(HF). In the Introduction the variation of threshold energies with incremental halogen substitution was analyzed. On the basis of trends for a single type of halogen substituent, E_0 for HF elimination from CF_2ClCH_3 was predicted to be slightly smaller than the barrier for HCl. Our most striking finding is that the rate for HCl elimination is 25 ± 4 times *faster* than the HF rate, which corresponds to an E_0(HCl) that is 14.5 ± 1.0 kcal/mol lower than the E_0 for HF loss. These mixed halo-substituted alkanes have different E_0 trends than for individually substituted haloalkanes. We will analyze these trends now in terms of the nature of the transition state.

Following Maccoll's proposal[43] of a polar transition state, it has been assumed that all the dehydrohalogenation transition states are similar with a slight positive charge on the carbon with the halogen (the α-carbon) and a small negative charge on the carbon with the hydrogen (the β-carbon). Alkyl groups (via hyperconjugation) and chloro substituents (via p-orbital resonance) are assumed to stabilize the α-carbon by releasing electrons to the positive center. However, the high electronegativity of a fluorine α-substituent causes a withdrawal of electrons, which destabilizes the transition state and raises the E_0's.[3,10,44] These interpretations that the variation in the threshold barriers arises from Cl and F substituents exerting different types of electronic effects are not consistent with our findings. For example, the E_0(HCl) for CF_2ClCH_3 is 55 kcal/mol, the same as for CH_2ClCH_3, indicating that the two additional fluorines do not alter the threshold barrier. The E_0(HF) for CF_2ClCH_3 is 69.5 kcal/mol, which is 8.5 kcal/mol higher than that for CF_2HCH_3 and the same as for CF_3CH_3. This suggests that a Cl substituent is no different than an F regarding its influence on E_0(HF). It appears that Cl or F substituents significantly raise the barrier for loss of HF but slightly decrease or have little effect on the barrier for loss of HCl. If all halogen substituents at the α-carbon exert the same type of inductive effect on the dehydrochlorination and dehydrofluorination transition states, then the different trends in the E_0's suggest that the polarity of the HCl transition state is different from that for the HF transition state. We will now access the validity of this proposal that the polarity of the two transition states differ.

A change of the dehydrohalogenation transition state as the *nature of the substituent* is varied has been proposed by Chuchani and co-workers[45] to account for thermal decomposition rates for a series of α-substituted ethyl chlorides. Kinetic data from pyrolysis of $ZCHClCH_3$ were treated by the linear free energy relationship using the Taft correlation. For the ethyl chlorides a large negative ρ^* value ($\rho^* = -3.58$) found for Z = alkyl groups fit a wide range of electron-releasing substituents. If Z was an electron-withdrawing group, then the Taft plots had an inflection point at Z = methyl and a small negative slope with $\rho^* = -0.46$. Chuchani felt this change in slope reflected a change in the polarity of the C–Cl bond in the HCl elimination transition state. The small negative ρ^* corresponds to a very slight polarization of the C–Cl bond when Z is an electron-withdrawing group, but the large negative ρ^* reflects a much greater charge density on the carbon and chlorine when Z is an alkyl group.

If Chuchani's view that the electronic nature of a substituent can change the ionic character of the transition state is correct, it seems reasonable that the nature of the halogen (the leaving group) may also alter the ionic character of the transition state. If little charge density is developing at the α-carbon in the HCl elimination transition state, then electron-withdrawing substituents would have minimal effect on the reaction rate. We find that replacement of two α-hydrogens of CH_2ClCH_3 with fluorine has little effect on the E_0(HCl); other work has shown that substitution of two Cl's for the α-hydrogens reduces the E_0(HCl) by only 5 kcal/mol. For pyrolysis of $ZCHClCH_3$ at 633 K, the rate for Z = Cl was a factor of only 2 faster than for Z = F and a factor of just 4 faster than for Z = H. The similarities in the rates for Z = H, Cl, and F again suggest that F or Cl substituents have little effect on the rate of HCl elimination. Our chemical acti-

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vation data and Chuchani's thermal activation results both suggest little charge separation in the C–Cl bond for the HCl elimination transition state. The slightly faster thermal decomposition rate when chlorines are present might be attributed to the increased steric size of Cl versus H or F.

We find that the HF threshold for CH_2FCH_3 increases 11.5 kcal/mol when one F and one Cl are inserted for the two α-hydrogens, and it is known that the E_0 increases a similar amount when the two α-hydrogens are replaced by fluorines.[10] For the ethyl fluorides, the C–F bond in the transition state must be much more polar than the C–Cl bond because electronegative substituent dramatically raise the activation energy for loss of HF.

An electrostatic model developed by Buckley and Rodgers[46] for calculation of enthalpies of formation of chloro- and fluoroalkanes provides evidence that the electrostatic character of the C–X bond is altered when X = F versus Cl. Buckley and Rodgers find that different polarization parameters for the C–X bond are needed to fit the experimental data. According to the model, the F carries a 35% greater charge than the chlorine.

Nature of the Substituent Effect. Is the effect exerted by Cl and F substituents at the α-carbon an inductive effect, a resonance effect, or a steric size effect? In general, the highly electronegative Cl and F both withdraw electrons with the F having the greater inductive effect. Alternatively, the Cl and F may donate electrons via a p-orbital resonance effect with the Cl having the greater tendency. With respect to the HX elimination transition states, it has been assumed that the net effect is that Cl donates and F withdraws electrons.[3,10,44] However, our results for elimination of HF from CF_2ClCH_3 indicate that Cl and F substituents behave similarly: they withdraw electrons. In addition, Chuchani's thermal activation rates for HCl elimination from $ZCHClCH_3$ shows that both Z = F and Cl fit the linear free energy line containing just polar substituents. This again suggests that both Cl and F withdraw electrons. Chuchani's thermal data show that one electronegative group on an α-carbon of the HCl transition state reduces the polarity of the C–Cl bond. Perhaps a second electronegative group further reduces the charge so that the α-carbon containing two polar substituents might be almost neutral. Therefore, no inductive or resonance effect would exist when HCl is lost from CF_2ClCH_3. In this case only the substituents steric volume would influence the rate so that Cl would tend to accelerate the rate more than fluorine or hydrogen. This is consistent with a slightly lower E_0(HCl) for both CH_3CHCl_2 and CH_3CCl_3 compared to CH_3CF_2Cl or CH_3CH_2Cl.

Correlation between the Bond Dissociation Energies and E_0. Successful RRKM models have a weakly bound hydrogen (C–H bond order near 0.1) and a C–X bond that is slightly ruptured (bond order near 0.9). Thus, the strength of the C–H bond and perhaps the C–X bond would directly influence the E_0.

When the α-hydrogens of fluoroethane are replaced by fluorine, the C–F bond dissociation energy increases markedly,[41] CH_2FCH_3 (107.5 kcal/mol) to CF_3CH_3 (124.8). The C–F BDE also rises as fluorines are added to methane.[41]. CH_3F (110.8 kcal/mol), CH_2F_2 (119.5), CHF_3 (127.5), CF_4 (130.8). The increase in the C–F BDE correlates with the increase of E_0(HF) as the number of F substituents increase; CH_3CH_2F has E_0(HF) = 58 kcal/mol and CH_3CF_3 has E_0(HF) = 68 kcal/mol. The effect of Cl substituents on the carbon–chlorine BDE of chloroethanes is not known, but chlorine substituents reduce the C–Cl BDE for the chloromethanes: CH_3Cl (83.7 kcal/mol), CH_2Cl_2 (80.9), $CHCl_3$ (77.6), CCl_4 (73.1).[42] This trend parallels the reduction in the E_0(HCl) as chlorines are added to chloroethane. However, fluorine substituents have a much smaller effect on both the E_0(HCl) and the C–Cl bond dissociation energy for the methanes: E_0(HCl) = 55 kcal/mol for both CH_3CH_2Cl and CH_3CF_2Cl and the BDE are CH_3Cl (83.7 kcal/mol), CH_2FCl (84.6), CHF_2Cl (87.5), and CF_3Cl (87.1).[41] It is interesting that these data also support the proposal that the polarity of the C–Cl and C–F bonds differ, at least for the activated molecules. Assuming that a larger BDE results from an increase in the ionic character of a bond, then these tendencies also suggest that the C–F bond is more ionic than the C–Cl bond.

For the C–H bond, the increase of 6.7 kcal/mol in the β-carbon C–H bond dissociation energy as two fluorines are added to the α-carbon of fluoroethane, vide ante., parallels the increase in the E_0(HF). Unfortunately, the influence of Cl substituents or of mixed-halogen substituents on the C–H BDE for a series of ethanes is not known. However, for the methanes, additional chlorines slightly reduce the C–H BDE; CH_3F (101.3 kcal/mol),[41] CH_2FCl (100.8 ± 1.3),[42] $CHFCl_2$ (98.9 ± 1.2),[42] and for the series CH_4 (105.1 kcal/mol),[41] CH_3Cl (100.8 ± 1.0),[42] CH_2Cl_2 (98.4 ± 1.2),[42] $CHCl_3$ (95.8 ± 1.0).[47] If the carbon–hydrogen BDE for the ethanes parallels the trend observed for the methanes, then the reduction in the C–H BDE correlates with the reduction of the E_0(HCl) for the chloroethanes. It is interesting that when one F is present and then two chlorines are substituted for the hydrogens of fluoromethane the C–H BDE decreases just 2.4 kcal/mol. However, when no fluorines are present and two chlorines are substituted for the hydrogens the decline is larger, 6.5 ($CH_4 \rightarrow CH_2Cl_2$) and 5.0 kcal/mol ($CH_3Cl \rightarrow CHCl_3$). Apparently, the presence of fluorine somewhat mitigates the tendency of the chlorines to reduce the carbon–hydrogen BDE; the same effect is observed in the trends of the E_0(HCl) for $CH_3CH_2Cl \rightarrow CH_3CCl_3$ (E_0 declines 5 kcal/mol) verses $CH_3CH_2Cl \rightarrow CH_3CF_2Cl$ (E_0's are similar when fluorines are present).

Substituent Effects at the β-Carbon. The current work with CF_2ClCH_3 focused on substituents effects at the α-carbon; however, any interpretation must be cognizant of trends in threshold barriers with substitution at the β-carbon. Alkylation at the β-carbon has the same, but considerably smaller effect as alkyl substitution at the α position; the E_0 is lowered. On the basis of the effects of Cl substituents on the HCl barrier and F substituents on the HF barrier, it appears that both F and Cl substituents on the β-carbon increase the E_0 for dehydrohalogenation.[3,10,44] Although little has been done with mixed haloalkanes, we have just completed a chemical activation study with CF_3CH_2Cl that shows the effect of β-chlorination is to also increase the HF threshold energy. Apparently, all halogen substituents exert a similar electronic effect at the β-carbon; they raise the E_0. Thus, our suggestion that all halogens at the α-carbon exert an inductive effect is reasonable. To explain substituent effects at the β-carbon it has been assumed[3,10,44] that a δ negative charge develops at the β-position. Halogens would have to provide electrons, and alkyl groups would have to remove electron density to explain the variation in the E_0's. This seems unlikely since the effect of these substituents is normally just reversed. Clearly, the variation in the threshold barriers as substituents are added to the β-carbon is not readily reconcilable with the effects at the α-carbon. Comparison of C–H and C–X bond dissociation energies with halogen substituents at the β-carbon would be of interest; unfortunately those data are not available.

Conclusions

Unimolecular elimination of HCl from chemically activated CF_2ClCH_3 was found to 25 ± 4 times faster than loss of HF. A similar branching ratio was found for CF_2ClCD_3, and the isotopic effect was 3.2 ± 0.9 for HCl/DCl and 3.0 ± 0.9 for HF/DF. Comparison of the isotope effect from a series of mono-, di-, and trisubstituted haloethanes suggests an incremental increase in k^H/k^D with increased halogenation. By matching RRKM and experimental rate constants, the threshold barriers were assigned as 55 ± 2 kcal/mol for HCl elimination and 69.5 ± 2 kcal/mol for ejection of HF. These threshold barriers are different than values predicted for CF_2ClCH_3 based on trends from a series of chloro- and fluoro-substituted ethanes. The fact that the α-halogen substituents raise the E_0(HF) and slightly reduce or had little effect on the E_0(HCl) may be due to a change in charge separation of the C–X bond in the transition state and not due to different types of electronic effects for the F versus Cl substituents. A tentative

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conclusion is that the C–X bond in the transition state changes from a nearly neutral C–Cl bond for HCl loss to a C–F bond that has significant charge separation between the C and the F when HF is eliminated. Trends in the carbon–hydrogen and the carbon–halogen bond dissociation energies as chlorines or fluorines are substituted for the hydrogens of haloethanes parallels the variation of the E_0(HCl) and E_0(HF), respectively.

Regardless of the reasons for the change in the E_0's with halogenation, it is clear that caution must be exercised when extrapolating trends in a set of data to predict properties of the chlorofluorocarbons. In addition, further experimental and theoretical work is certainly needed to help unravel the intricacies of substituents effects at both the α- and β-carbons. To this end we have begun work with chemically activated $CFCl_2CH_3$ to determine if the E_0's for loss of HCl and HF agree with the above conclusions. Additional data on the strength of C–H and C–X bonds for the haloethanes would be very useful in verifying the correlation between E_0(HX) and the bond dissociation energies.

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Appendix

The average energy, $\langle E \rangle$, for CF_2ClCH_3 was calculated from the enthalpies of formation of CF_2ClCH_3, CF_2Cl, and CH_3. The $\Delta H_f(CF_2ClCH_3) = -128.8$ kcal/mol, recommended by Buckley and Rogers,[46] was used, which is in good agreement with the experimental value of −126.6 kcal/mol of Papina and Kolesov.[48] Conversion to 0 K gave $\Delta H_f{}^\circ = -125.8$ kcal/mol. For the methyl radical the ΔH_f at 0 K is 35.9 kcal/mol.[49] The $\Delta H_f{}^{298}$ (CF_2Cl) was estimated from the C–H bond dissociation energy of CF_2ClH and the ΔH_f of the H atom and CF_2ClH. The D(R–H) was determined from trends in the dissociation energies of several halomethanes reported by Tschuikow-Roux and Paddison.[42] The estimated $D_0{}^{298}$ (CF_2Cl–H) = −101 kcal/mol together with $\Delta H_f{}^{298}$ (CF_2ClH) = −115.1 kcal/mol[50] gave $\Delta H_f{}^{298}(CF_2Cl) = -66.2$ kcal/mol. This value is somewhat lower than the −64.2 kcal/mol (298 K) reported by Kerr[51] but is in excellent agreement with −66.5 kcal/mol (298 K) estimated by Lee and co-workers[52] from analysis of trends in the carbon–chlorine bond dissociation energies of chlorofluoromethanes. Conversion to 0 K gave $\Delta H_f{}^\circ(CF_2Cl) = -65.3$ kcal/mol. The $\Delta H_{rxn}(CF_2ClCH_3)$ was calculated to be −96.4 kcal/mol. Finally, the $\langle E \rangle$ of 101.1 kcal/mol was obtained by combining $\Delta H_{rxn}(CF_2ClCH_3)$ with a 1 kcal/mol activation energy for radical combination and 3.7 kcal/mol thermal energy of CF_2ClCH_3.

Similarly, the $\langle E \rangle$ value of 102 kcal/mol was obtained for $CF_2Cl + CD_3 \rightarrow CF_2ClCD_3$ by assuming that $\Delta H_f{}^{298}(CF_2ClCD_3) = \Delta H_f{}^{298}(CF_2ClCH_3)$, using $\Delta H_f{}^\circ(CD_3) = 35.9$ kcal/mol[48] and the same thermal energy as CF_2ClCH_3.

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Theory of Charge-Transfer Spectra in Frozen Media

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Absorption and fluorescence maxima of charge-transfer spectra in frozen media are treated, noting that only some of the nuclear motions for liquid medium are frozen in corresponding solid or glassy phase. Account is taken of the fact that the conditions under which the static dielectric constant of the frozen phase is measured do not usually correspond to those in which the initial state of the solute system is prepared. Expressions for the maxima are obtained in terms of the optical and static dielectric constants of the liquid and frozen (solid or glassy) phases. Comparison of Stokes shifts $h\nu_a - h\nu_f$ at conventional fluorescence times in frozen media with Stokes shifts at picosecond or subpicosecond times in liquid media would be of interest.

Introduction

The effects of polarity of the solvent on charge-transfer (CT) spectra have been of considerable interest in recent decades. Molecules in which the intramolecular charge transfer is largely associated with a change of dipole moment[1,2] have been the subject of intensive study, as have CT spectra of mixed-valence complexes.[3,4] In the most frequently used theoretical treatments for these systems, the solvent has been treated as a dielectric continuum, characterized by its static and optical dielectric constants.[1-4] The effect of the polar solvent medium on the spectra has been described, applying the Franck–Condon principle to the spectral transition.[1-4] The studies have normally been for liquid media.

Recently, a very interesting study was published by Hammack et al.[5] on the charge-transfer spectrum of a mixed-valence complex in a frozen medium

$$(bpy)_2ClRu^{II}(pz)Ru^{III}Cl(bpy)_2{}^{3+} \xrightarrow{h\nu_{CT}} (bpy)_2ClRu^{III}(pz)Ru^{II}Cl(bpy)_2{}^{3+} \qquad (1)$$

where bpy is 2,2′-bipyridyl and pz is pyrazine. These authors varied the dielectric constant of the existing phase in the vicinity of the liquid–solid phase transition point of the solvent, by varying the static pressure. The phase transition itself was accompanied by a marked change in the static dielectric constant in the case

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[†] Contribution No. 8067.

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