Threshold Energies and Unimolecular Rate Constants for Elimination of HF from Chemically Activated $CF_3CH_2CH_3$ and $CF_3CH_2CF_3$: Effect of CH_3 and CF_3 Substituents at the *β*-Carbon and Implications about the Transition State

Heather A. Ferguson, John D. Ferguson, and Bert E. Holmes*

Department of Chemistry, Lyon College, Batesville, Arkansas 72501

Received: September 2, 1997; In Final Form: November 17, 1997

Chemically activated $CF_3CH_2CF_3$ was prepared with 104 kcal/mol of internal energy by the combination of CF_3CH_2 and CF_3 radicals, and chemically activated $CF_3CH_2CH_3$ was prepared with 101 and 95 kcal/mol by combination of CF_3 and CH_2CH_3 radicals and by combination of CF_3CH_2 and CH_3 radicals, respectively. The experimental rate constants for unimolecular 1,2-dehydrofluorination were 1.2×10^5 s^{-1} for $CF_3CH_2CF_3$ and 3.2×10^6 s^{-1} for $CF_3CH_2CH_3$ with 95 kcal/mol and 2.0×10^7 s^{-1} with 101 kcal/mol of energy. Fitting the calculated rate constants for HF elimination from RRKM theory to the experimental values provided threshold energies, E_0, of 73 kcal/mol for $CF_3CH_2CF_3$ and 62 kcal/mol for $CF_3CH_2CH_3$. Comparing these threshold energies to those for CF_3CH_3 and CF_3CH_2Cl illustrates that replacing the hydrogen of CF_3CH_3 with CH_3 lowers the E_0 by 6 kcal/mol and replacing with CF_3 or Cl raises the E_0 by 5 and 8 kcal/mol, respectively. The CF_3 substituent, an electron acceptor, increases the E_0 an amount similar to Cl, suggesting that chlorine substituents also prefer to withdraw electron density from the *β*-carbon. As the HF transition state forms, it appears that electron density flows from the departing hydrogen to the *β*-carbon and from the *β* to the α-carbon, to the α-carbon from its substituents, but the α-carbon releases most of the incoming electron density to the departing fluorine. The present work supports this scenario because electron-donating substituents, such as CH_3, on either carbon would reduce the E_0 as they aid the flow of negative charge, while electron-withdrawing substituents such as Cl, F, and CF_3 would raise the E_0 for HF elimination because they hinder the flow of electron density.

Introduction

For several years we have been measuring[1−5] unimolecular rate constants for the 1,2-dehydrohalogenation of chemically activated hydrofluorocarbons and hydrochlorofluorocarbons, and by fitting rate constants calculated using the RRKM theory to the experimental values, threshold energies, E_0's, have been determined. By altering substituents and measuring their effect on the rate constant and on the threshold energy barrier, it should be possible to better understand the flow of electron density as the four-centered transition state for chloro- and fluoroalkanes forms and also to understand whether substituents act as electron donors or acceptors.

Recent work[2−5] by this laboratory for HF elimination has shown that CF_3, Cl, and F substituents at the α-carbon all raise the threshold energy, and because CF_3 accepts electron density, the Cl and F substituents presumably have a similar inductive effect. The α-carbon contains the halogen that is eliminated, and in this paper, it is the first carbon in the chemical formula. According to theoretical calculations by Toto, Pritchard, and Kirtman[6] for HF elimination from hydrofluorocarbons, the α-carbon acquires electron density from the substituents and from the *β*-carbon as the transition state forms. This might suggest, contrary to observations, that electron-withdrawing substituents would help disperse the electron density accumulating on the α-carbon, thus stabilizing the transition state and lowering the E_0. However, the calculations also predict that electron density flows from the substituents to the α-carbon and to the departing F, and this suggests that an electron-withdrawing group would hinder the transfer of electron density to the α-carbon, thereby raising the threshold energies. This latter view is consistent with experimental observations[2−5] that CF_3, Cl, and F increase E_0's, but a CH_3 group has the opposite effect. For CH_2FCH_3, CHF_2CH_3, and CF_3CH_3, the calculations[6] also predict that the *β*-carbons acquire electron density, probably from the attached H's, and transfer a portion of this charge to the α-carbon as the HF departs; the changes in atomic charges on the *β*-carbon are $-0.03e$, $-0.07e$, and $-0.09e$, respectively. Although the ab initio results[6] did not test the effect of *β*-carbon substituents, because both carbons acquire electron density it is reasonable to speculate that *β*-carbon and α-carbon substituents would have the same effect on the E_0.

From the E_0(HF) for CF_3CH_3 (68 kcal/mol)[7] and CF_3CH_2Cl (76 kcal/mol)[3] it is seen that replacing an H with a Cl at the *β*-carbon raises the E_0. The E_0(HF)'s for two series of hydrofluoroethanes show the same general trends for successive fluorine for hydrogen substitution at the *β*-carbon: CH_2FCH_3 (57 kcal/mol),[7,8] CH_2FCH_2F (61.5),[9] and CH_2FCHF_2 (68)[10−12] and CHF_2CH_3 (61),[13] CHF_2CH_2F (68),[10−12] and CHF_2CHF_2 (74.5).[10,12] This illustrates that, with one F at the α-carbon, successive substitution at the *β*-carbon raises the E_0 by 4.5−6.5 kcal/mol and, with two F's at the α-carbon, the E_0 increases by about 7 kcal/mol. It appears that additional fluorines at the α-position magnify the effect of F substituents at the *β*-position. The ab initio calculations[6] support this supposition because the change in charge at the *β*-carbon is most pronounced, $-0.09e$, when there are three F's at the α-carbon. This suggests that a CF_3CH_2X series (X = substituent) would be the best to investigate because the effect of *β*-carbon substituents should be the most pronounced. Although F and Cl substituents on the *β*-carbon increase the E_0(HF), it is not known whether they

S1089-5639(97)02854-5 CCC: $15.00

are donating or withdrawing electron density as the transition state forms because F and Cl can function in either manner. To determine the behavior of the F and Cl, the H at the β-carbon will be replaced with a CF_3 substituent, an electron withdrawer, and a CH_3, an electron donor. In addition, this comparison should provide information about the development of atomic charges on the carbons as the transition state forms. In this paper we will report unimolecular rate constants and E_0's for HF elimination from $CF_3CH_2CF_3$ ($X = CF_3$) and from $CF_3CH_2CH_3$ ($X = CH_3$) that will ascertain the electronic behavior of the F and Cl substituents at the β-carbon. This information should also be a useful benchmark when ab initio calculations appear that test the effect of β-carbon substituents.

Both hydrofluoropropanes were prepared by chemical activation, and two different reactions were used to produce $CF_3CH_2CH_3$ at two different levels of energy. The chemically activated $CF_3CH_2CH_3$* (the asterisk denotes chemical activation), containing 95 kcal/mol of internal energy, was formed by the combination of CF_3CH_2 and CH_3 radicals produced from the photolysis of CF_3CH_2I and CH_3I in the presence of Hg_2I_2.[14] The important reaction channels are as follows:

$$2CF_3CH_2I + Hg_2I_2 \xrightarrow{h\nu} 2CF_3CH_2\cdot + 2HgI_2 \qquad (1a)$$

$$2CH_3I + Hg_2I_2 \xrightarrow{h\nu} 2CH_3\cdot + 2HgI_2 \qquad (1b)$$

$$\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3 \qquad (2)$$

$$CF_3CH_2\cdot + CF_3CH_2\cdot \rightarrow CF_3CH_2CH_2CF_3{}^* \qquad (3)$$

$$CF_3CH_2\cdot + \cdot CH_3 \rightarrow CF_3CH_2CH_3{}^* \qquad (4)$$

Reaction 4 produced chemically activated $CF_3CH_2CH_3$* which eliminated HF (reaction 5a) or, at increased pressures, was stabilized through collision (reaction 5b).

$$CF_3CH_2CH_3{}^* \xrightarrow{k_{HF}} CF_2{=}CHCH_3 + HF \qquad (5a)$$

$$\xrightarrow{k_M[M]} CF_3CH_2CH_3 \qquad (5b)$$

Photolysis of CH_3CH_2I and CF_3I produced CH_3CH_2 and CF_3 radicals that combined to give $CF_3CH_2CH_3$, containing 101 kcal/mol, reaction 6. For simplicity, the self-reactions of ethyl or CF_3 radicals are not shown.

$$CF_3\cdot + \cdot CH_2CH_3 \rightarrow CF_3CH_2CH_3{}^* \qquad (6)$$

The decomposition or stabilization of $CF_3CH_2CH_3$* is the same as shown in reactions 5.

Reaction 7 is the preparation of chemically activated $CF_3CH_2CF_3$ containing 104 kcal/mol of internal energy, which is formed by photolysis of CF_3CH_2I and CF_3I. The unimolecular decomposition of $CF_3CH_2CF_3$* is shown in reaction 8a.

$$CF_3\cdot + \cdot CH_2CF_3 \rightarrow CF_3CH_2CF_3{}^* \qquad (7)$$

$$CF_3CH_2CF_3{}^* \xrightarrow{k_{HF}} CF_3CH{=}CF_2 + HF \qquad (8a)$$

$$\xrightarrow{k_M[M]} CF_3CH_2CF_3 \qquad (8b)$$

The ratio of the yield of the decomposition (D) products from reaction 5a or 8a and the stabilization (S) product from reaction 5b or 8b plotted versus inverse pressure should produce a linear relationship with an intercept of zero. The slope of the D/S versus 1/P plot equals k_{HF}/k_M, which is converted to k_{HF} by calculation of k_M using collision theory.

Experimental Section

For the $CF_3CH_2CH_3$ chemical activation study, vessels with a volume range of 14.85−2115.4 cm^3 containing 44.6−89.8 μmol of CF_3I and CH_3CH_2I or CH_3I and CF_3CH_2I were photolyzed 5−120 min at room temperature using a high-pressure Oriel 6137 mercury lamp. The Pyrex vessels contained Hg_2I_2 which removes iodine atoms to aid in the production of halocarbon radicals.[14] All samples were prepared on a grease-free vacuum line using an MKS 270 electric manometer. A Perkin-Elmer 3920 GC equipped with a flame ionization detector and an $^1/_8$ in. by 2 m stainless steel Porapak R column was used for product analysis. An initial GC temperature of 60 °C followed by immediate temperature programming of 2 °C/min to a final temperature of 210 °C was used for both methods of activating $CF_3CH_2CH_3$. For the CF_3I and CH_3CH_2I system, elution times (in minutes) were generally as follows: CF_3CF_3 (4.5), C_2H_6 (5.2), $CH_2{=}CH_2$ (5.2), $CF_2{=}CHCH_3$ (17), $CF_3CH_2CH_3$ (23), CF_3I (28), C_4H_{10} (30), and CH_3CH_2I (58). The C_2H_6 and $CH_2{=}CH_2$ arise from the disproportionation reaction between two ethyl radicals. For the CH_3I with CF_3CH_2I system, elution times (in minutes) were typically C_2H_6 (5.2), $CF_2{=}CHCH_3$ (17), $CF_3CH_2CH_3$ (23), $CF_3CH_2CH_2CF_3$ (37), CH_3I (43), and CF_3CH_2I (49). The data were collected and integrated with a Shimadzu Chromatopac CR5A integrator.

Products were identified by comparison of GC retention times with authentic samples, and the purity and identity were verified by a Hewlett-Packard 5890/5791 GC/MS equipped with a 50 m PONA capillary column, except for $CF_2{=}CHCH_3$. The $CF_2{=}CHCH_3$ was identified by its expected pressure dependency of a chemically activated, unimolecular decomposition system and by the following mass spectrum: ($C_3H_3F_2{}^+$) m/z = 77 (RA = 100%), ($C_3H_4F_2{}^+$) 78 (60.4%), (CF_2H^+) 51 (37.3%), ($C_3F_2H^+$) 75 (18.6%), ($C_3H_2F_2{}^+$) 76 (14.1%), and (CF^+) 31 (7.3%).

Because an authentic sample of $CF_2{=}CHCH_3$ was unavailable, the calibration factor for $[CF_2{=}CHCH_3]/[CF_3CH_2CH_3]$ was estimated by comparing $CF_3CH{=}CH_2$ and $CF_3CH{=}CF_2$ with $CF_3CH_2CH_3$. The calibration factors for $[CF_3CH{=}CH_2]/[CF_3CH_2CH_3]$ and $[CF_3CH{=}CF_2]/[CF_3CH_2CH_3]$ were 0.953 ± 0.017 and 1.07 ± 0.07, respectively, using six trials of five mixtures of the products and reactants to replicate reaction mixtures. These values were then averaged to obtain the estimated calibration factor of 1.01 for $[CF_2{=}CHCH_3]/[CF_3CH_2CH_3]$.

For the chemically activated $CF_3CH_2CF_3$ system, the CF_3 and CF_3CH_2 radicals were generated by photolysis of about 12 μmol each of CF_3I and CF_3CH_2I in Pyrex vessels containing Hg_2I_2 and ranging in volume from 11.31 to 2115.4 cm^3. Samples were treated as described for the $CF_3CH_2CH_3$ systems, except that the photolysis times varied from 2 to 45 min. Reaction mixtures were analyzed using a Shimadzu GC-14A gas chromatograph equipped with 1/8" x 2 m Haysep A column coated with 5% Ni. With an initial temperature of 80 °C for 5 min followed by temperature programming at 2 °C/min to a final temperature of 167 °C, the retention times were C_2F_6 (2.5), $CF_2{=}CHCF_3$ (19), CF_3I (27), $CF_3CH_2CF_3$ (32), $CF_3CH_2CH_2CF_3$ (44), and CF_3CH_2I (70). A Shimadzu Chromatopac CR5A integrator measured the product yields. Reaction products were identified by comparing the GC retention times and mass spectra

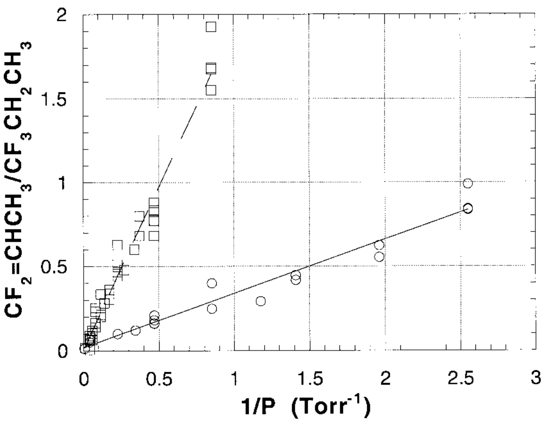

Figure 1. A plot of [CF_2═$CHCH_3$]/[$CF_3CH_2CH_3$] versus reciprocal pressure for the four-centered elimination of HF from chemically activated $CF_3CH_2CH_3$ with 95 kcal/mol (circles) and 101 kcal/mol (squares) of internal energy. The slope is 1.94 Torr, the intercept is 0.004 37, and the correlation coefficient is 0.983 at the higher energy, and the values are 0.321 Torr, 0.0188, and 0.979, respectively, for $CF_3CH_2CH_3$ with 95 kcal/mol of energy.

with commercial samples. The GC detector calibration factor for [CF_3CH═CF_2]/[$CF_3CH_2CF_3$] was 1.0085 ± 0.0110.

Results and Discussion

In this section the experimental unimolecular rate constants will be discussed first, and they will be converted to units of s^{-1} using collision cross sections. Next the average energy of the chemically activated molecules will be calculated, and the RRKM model will be developed. Then the threshold energies will be estimated by iteration of the RRKM calculations until the calculated and experimental rate constants agree at the energy of activation. The ab initio calculations of Toto et al.[6] will then be summarized for CF_3CH_3, and the threshold energies for a series of CF_3CH_2X will be compared to determine the effect of substituents on the threshold energies. Finally, the trends in E_0's will be analyzed to help understand the nature of the 1,2-HF elimination transition state.

The unimolecular rate constants for elimination of HF from $CF_3CH_2CH_3$ and $CF_3CH_2CF_3$ were determined from the D/S versus 1/P plots. Figure 1 has a slope of 1.9 Torr for loss of HF from $CF_3CH_2CH_3$ containing 101 kcal/mol of internal energy, $\langle E \rangle$, and a slope of 0.32 Torr for $CF_3CH_2CH_3$ when $\langle E \rangle = 95$ kcal/mol. Figure 2 has a slope of 0.0117 Torr for loss of HF from $CF_3CH_2CF_3$. Rate constants in pressure units were converted to s^{-1} using temperature-independent collision diameters for CH_3I (5.0 Å), CF_3I (5.6 Å), CH_3CH_2I (5.6 Å), CF_3CH_2I (6.2 Å), $CF_3CH_2CH_3$ (5.6 Å), and $CF_3CH_2CF_3$ (5.7 Å). Collision diameters for CF_3I and CH_3I are known,[2,3] and the collision diameters for the other species were estimated by determining the increase in collision diameters for the replacement of H by an I (+1.21 Å), by substitution of a CF_3 group for a CH_3 group (+0.6 Å), and by the effect of an additional CH_2 in a homologous series of alkanes (+0.55 Å).[15] The k_{HF}'s for $CF_3CH_2CH_3$ with $\langle E \rangle = 101$ and 95 kcal/mol and for $CF_3CH_2CF_3$ were 2.0×10^7, 3.2×10^6, and 1.2×10^5 s^{-1}, respectively.

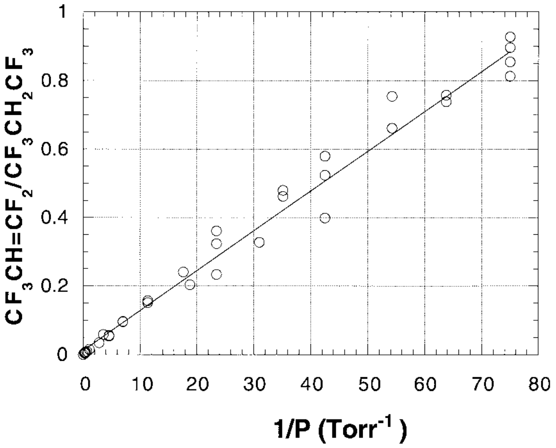

Figure 2. A plot of [CF_3CH═CF_2]/[$CF_3CH_2CF_3$] versus reciprocal pressure for the four-centered elimination of HF from chemically activated $CF_3CH_2CF_3$; the slope is 0.0117 Torr, the intercept is 0.0118, and the correlation coefficient is 0.991.

TABLE 1: Experimental Unimolecular Rate Constants for 1,2-HF Elimination from CF_3CH_2X (X = H, Cl, CH_3, and CF_3), the Average Energy of the Chemically Activated Molecule, and the Threshold Energy

molecule	$\langle E \rangle$ (kcal/mol)	k_{HF} (s^{-1})	E_0 (kcal/mol)
CF_3CH_3[a]	102	3.7×10^8	68
CF_3CH_2Cl[b]	97.5	2.8×10^6	76
$CF_3CH_2CH_3$[c]	95	3.2×10^6	62
$CF_3CH_2CH_3$[c]	101	2.0×10^7	62
$CF_3CH_2CF_3$[c]	104	1.2×10^5	73

[a] Reference 7. [b] Reference 3. [c] This work.

The average energy of the chemically activated fluoropropanes, $\langle E \rangle$, is the enthalpy for reactions 4, 6, and 7 at 0 K plus the thermal energy of the reactants. The enthalpy of formation at 298 K for $CF_3CH_2CH_3$ has not been reported so it was estimated as −181 kcal/mol from group additivity schemes,[16] and adjustment to 0 K gave −175.5 kcal/mol. At 298 K the enthalpy of formation for $CF_3CH_2CF_3$ has been measured[17] as −333.5 kcal/mol, and adjustment to 0 K gave −329.9 kcal/mol. For the methyl radical the $\Delta H_f^o(0\ K) = 35.6$ kcal/mol,[18] and for the ethyl radical the $\Delta H_f^o(0\ K) = 31.0$ kcal/mol.[19] Data recommended by Rodgers[20] were adopted for the CF_3 and the CF_3CH_2 radicals; −111.06 and −123.5 kcal/mol at 298 K were corrected to −110.4 and −120.9 kcal/mol at 0 K, respectively. The $\Delta H^o_{rxn}(0\ K)$ were −90.2 and −96.1 kcal/mol for reactions 4 and 6, respectively; addition of 4.8 kcal/mol thermal energy for the two radical reactants gives an $\langle E \rangle = 95$ kcal/mol for reaction 4 and $\langle E \rangle = 100.9$ kcal/mol, which was rounded to 101 kcal/mol, for reaction 6. The $\Delta H^o_{rxn}(0\ K)$ was −98.6 kcal/mol for reaction 7; addition of 4.9 kcal/mol thermal energy gives $\langle E \rangle = 103.5$ kcal/mol, which was rounded to 104 kcal/mol. An $\langle E \rangle$ value exceeding 100 kcal/mol for the fluoropropanes agrees with recent ab initio calculations[21,22] of the carbon−carbon bond dissociation energies for a series of fluoroethanes that predicted the increased ionic character in the C−C bond for CF_3CH_3 would cause the dissociation energy to be 6[21] to 12[22] kcal/mol higher than for ethane. We also note that the $\langle E \rangle$ for reaction 6 is 5.9 kcal/mol higher than that for reaction 4, which agrees with the ab initio predictions.[21,22]

A goal is to extract the threshold energies for 1,2-HF elimination by comparing experimental unimolecular rate constants with rate constants calculated using the RRKM theory and then compare the E_0's for a series of CF_3CH_2X molecules (X = H, Cl, CF_3, and CH_3) to determine the effect of β-carbon substituents on the E_0's. To our knowledge, thermal activation experiments have not been reported for $CF_3CH_2CF_3$ and $CF_3CH_2CH_3$ so RRKM models were developed and adjusted to a common thermal preexponential factor (partition function form) of $(9 \pm 1) \times 10^{12}$ s^{-1} per reaction path at 800 K (Table 2). Models previously developed for the other CF_3CH_2X systems, CF_3CH_2Cl[3] and CF_3CH_3,[7] had been parametrized to a thermal preexponential factor within the expected limits so the E_0's from

TABLE 2: Summary of Experimental Rate Constants and RRKM Models for 1,1,1,3,3,3-Hexafluoropropane and 1,1,1-Trifluoropropane

	molecule $CF_3CH_2CF_3$	activated complex, elimination of HF	molecule $CF_3CH_2CH_3$	activated complex, elimination of HF
vibrational frequencies, cm^{-1} and (degeneracies)	3011 (2)	3028 (1)	2954 (5)	2949 (4)
	1272 (9)	1352 (5)	1340 (10)	1376 (8)
	879 (3)	974 (6)	920 (4)	917 (6)
	576 (6)	717 (3)	568 (3)	605 (3)
	332 (4)	530 (4)	349 (3)	349 (3)
	128 (2)	320 (5)	241 (1)	241 (1)
	66 (1)	100 (2)	215 (1)	215 (1)
moments of inertia $I^{\ddagger}/I$		0.94		0.969
reaction path degeneracy[a]		8		4
preexponential factor,[b] s^{-1}		9.0×10^{12}		9.0×10^{12}
E_o, kcal/mol		73		62
$\langle E\rangle$, kcal/mol		104		95, 101
k_a(exptl), s^{-1}		1.2×10^5		3.2×10^6, 2.0×10^7
k_a(calcd), s^{-1}		1.3×10^5		3.7×10^6, 1.2×10^7

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

these models were accepted without modification. Vibrational frequencies for $CF_3CH_2CH_3$ were estimated from $CH_3CH_2CH_3$,[23,24] $CF_3CF_2CF_3$,[25] $CH_2FCH_2CH_3$,[26] and $CF_3CH_2CF_3$.[27,28] The vibrational frequencies for $CF_3CH_2CF_3$ are known,[27,28] and the frequencies for the four-member transition states were assigned from previous models[2-5] with the ring puckering adjusted to give a preexponential factor within the desired range. A torsional model was assumed giving reaction path degeneracies of 8 for $CF_3CH_2CF_3$ and 4 for $CF_3CH_2CH_3$, and an exact count was used for the sum of states for the activated complexes. Table 1 contains experimental rate constants, the $\langle E\rangle$'s, and the E_0's for the CF_3CH_2X series.

The calculated rate constant matched the experimental values with $E_0(HF) = 62$ kcal/mol for $CF_3CH_2CH_3$ at both energies of activation, and with $\langle E\rangle = 104$ kcal/mol for $CF_3CH_2CF_3$ the $E_0(HF) = 73$ kcal/mol (see Tables 1 and 2). The largest source of error is likely the thermochemistry used to calculate the $\langle E\rangle$, and the reported accumulated uncertainty is ±4 kcal/mol. If the $\langle E\rangle$'s are lowered by 4 kcal/mol, then the calculated rate constant would be too low by about a factor of 1.9. To restore agreement between the calculated and the experimental rate constants, the threshold energies would need to be reduced by 2 kcal/mol, which increases the RRKM rate by a factor of 2.3. On the basis of this analysis, we estimate the uncertainty in E_0's is ±2 kcal/mol. Cadman et al.[29] also developed an RRKM model for $CF_3CH_2CH_3$ and compared the calculations to unpublished experimental work for the formation of $CF_3CH_2CH_3$ by radical combination and by insertion of a CH_2 into the C−H bond of CF_3CH_3. Their RRKM model is based on a thermal preexponential factor considerably outside the range we adopted, and their thermochemistry gives $\langle E\rangle$'s that differ by 5 kcal/mol from the present results, so their higher E_0 (68 kcal/mol) is not unexpected.

Toto et al.[6] calculated molecular and transition-state atomic charges for CF_3CH_3 and for the four-centered HF-elimination transition state. The charge on the β-carbon also includes the atomic charges carried by the two hydrogens which are not being eliminated. It is predicted that electron density flows from the departing H to the β-carbon, from the β-carbon to the α-carbon, from the fluorine substituent to the α-carbon, and from the α-carbon to the F being eliminated. Although the α-carbon and the β-carbon maintain different signs in their partial charges, both the α-carbon and the β-carbon acquire more electron density than they donate, giving them a net gain in electron density of $-0.09e$ and $-0.12e$, respectively. These results predict that although fluorine substituents are electron-withdrawing and maintain a partial negative charge, they actually provide electron density to the α-carbon as the transition state forms.

At the α-carbon, the experimental E_0's are increased by 7−8.5 kcal/mol as an H from CHF_2CH_3 ($E_0 = 61$ kcal/mol)[7,8] is replaced by an F (CF_3CH_3, $E_0 = 68$ kcal/mol),[7] is replaced by a CF_3 ($CF_3CF_2CH_3$, $E_0 = 68.5$ kcal/mol),[5] or is replaced by a Cl ($CClF_2CH_3$, $E_0 = 69.5$ kcal/mol),[2] suggesting that F's, CF_3's, and Cl's exhibit similar behaviors at the transition state. Since a CF_3 group is known to be electron accepting, the F and Cl substituents on the α-carbon must also tend to withdraw electron density. Replacing the H from CHF_2CH_3 with a CH_3 ($CH_3CF_2CH_3$, $E_0 = 54$ kcal/mol)[5] lowers E_0 by 7 kcal/mol, which is consistent with methyl's ability to donate electron density. At the α-carbon it appears the magnitude of the effect of an electron donor (CH_3) is nearly equal to the effect of the electron acceptors (CF_3, F, or Cl). The calculation[6] predicts that fluorine substituents on the reactant are strong electron acceptors (each F of CF_3CH_3 contains $-0.31e$), but chlorine substituents are nearly neutral or very slightly electron donors (each Cl of CCl_3CH_3 contains $+0.01e$ or $+0.02e$). Apparently, the Cl and F substituents exert similar inductive effects as the transition state forms, even though they have different electronic behavior in the reactant. When relating variation of the E_0's to the calculated atomic charges on the carbon skeleton, it is assumed that the substituents exert mainly an inductive, resonance, or other electronic effect on the atomic charges that develop as the transition state is formed from the reactant.

At the β-carbon, the replacement of the H by a CF_3 or by a Cl substituent for the series of CF_3CH_2X molecules (see Table 1) raised the threshold energy by 5 and 8 kcal/mol, respectively, and a CH_3 substituent lowered the threshold energy by 6 kcal/mol. The effect of the CF_3 group on the E_0 is in the same direction and of similar magnitude as a Cl substituent, suggesting that they attempt to remove electron density from the β-carbon. It does appear that at the β-carbon a Cl substituent might have a slightly greater effect than a CF_3. The influence of a β-carbon fluorine substituent on the E_0 for CF_3CH_2X (X = F) has not been determined, but the series of fluoroethanes presented in the Introduction suggests that fluorine for hydrogen substitution for a series of mono- and difluoroethanes raises the E_0 by 4−7 kcal/mol. The ab initio calculations[6] predict that both the α- and β-carbons acquire electron density with a net gain that is nearly identical ($-0.09e$ and $-0.12e$, respectively), and this is in agreement with the experimental observations that the magnitude of the effect on E_0 by electron-donating or -accepting substituents are similar at each carbon. The ab initio calculations[6] focused on substituent effects at the α-carbon and did not test β-carbon substituents; however, because methyl, chloro, and trifluoromethyl substituents cause similar changes in the E_0's at both the α- and β-carbons, it is tempting to speculate that β-carbon substituents are also forced to provide electron density as the HF departs.

A number of issues about the transition state remain. It would be useful to have ab initio calculations that determined whether CH_3 and CF_3 substituents at the α- and β-carbons would produce E_0's consistent with the experimental results. Also, it would be helpful to have calculations for the series of CF_3CH_2X molecules, listed in Table 1, that address the flow of electron density for β-carbon substituents and that determine whether a CF_3 substituent actually releases electron density to the carbon skeleton as the HF departs. It would be interesting to experimentally measure if the effect of a methyl substituent is counterbalanced by an electron acceptor such as CF_3, F, or Cl or if the effect of one type of substituent is dominant. It would also be interesting to measure whether experimental results for HCl loss are similar to those found for HF elimination when CH_3 and CF_3 substituents are present at the α- or β-carbons. We have begun to further experimentally and theoretically explore these and other issues regarding the 1,2-dehydrohalogenation reaction.

In summary, we have measured unimolecular rate constants for 1,2-HF elimination from chemically activated $CF_3CH_2CH_3$ and $CF_3CH_2CF_3$ and found that replacement of the H of CF_3-CH_3 with a methyl substituent lowers the threshold energy barrier by about 6 kcal/mol while replacement with a CF_3 substituent raises the barrier by about 5 kcal/mol. The Cl and F substituents have the same effect on the E_0 as a CF_3 group, suggesting halogen substituents would also attempt to remove electron density from the β-carbon. The picture of the HF elimination transition state that emerges for CF_3CH_3 is one where electron density flows to the β-carbon from the departing hydrogen and from its other substituents. A portion of this charge is transferred from the β-carbon to the α-carbon. The α-carbon also receives electron density from the electron-rich fluorine substituents, but the α-carbon releases most of this electron density to the departing fluorine. The present experimental results are consistent with this movement of electron density because electron-donating substituents, such as CH_3, on either carbon would aid the flow of negative charge and reduce the E_0, while Cl, F, and CF_3, which are electron-withdrawing substituents, would hinder the flow of electron density and raise the threshold energy for HF elimination. This view is also consistent with a previous suggestion[30] that the 1,2-elimination is a stepwise process: first the H is rapidly transferred to a lone pair on the departing F, the sp^3 hybridized carbons begin to relax to an sp^2 geometry, and then the F recoils from the α-carbon bringing the H with it. During this stepwise process electron density might flow to the β-carbon as the H moves to the lone pair on the F, then to the α-carbon, and finally to the departing F. This picture was suggested[30] to account for both the relative large release of energy to translational motion and the H/D kinetic isotope effect. A process where the first step is repulsion between the F and the α-carbon causing the F to drag the H along as it departs is also possible, but it is not clear this would reproduce the observed isotope effect.

Acknowledgment. We are pleased to acknowledge financial support provided by the National Science Foundation (CHE-9508666) and the Arkansas-NASA EPSCoR Program.

References and Notes

(1) Paisley, S. D.; Holmes, B. E. *J. Phys. Chem.* **1983**, *87*, 3042.

(2) Jones, Y.; Holmes, B. E.; Duke, D. W.; Tipton, D. L. *J. Phys. Chem.* **1990**, *94*, 4957.

(3) Rakestraw, D. J.; Holmes, B. E. *J. Phys. Chem.* **1991**, *95*, 3968.

(4) McDoniel, J. B.; Holmes, B. E. *J. Phys. Chem.* **1996**, *100*, 3044.

(5) McDoniel, J. B.; Holmes, B. E. *J. Phys. Chem. A* **1997**, *101*, 1334.

(6) Toto, J. L.; Pritchard, G. O.; Kirtman, B. *J. Phys. Chem.* **l994**, *98*, 8359.

(7) Chang, H. W.; Craig, N. L.; Setser, D. W. *J. Phys. Chem.* **1972**, *76*, 954.

(8) Cadman, P.; Day, M.; Trotman-Dickenson, A. F. *J. Chem. Soc. A* **1970**, 2498.

(9) Kerr, J. A.; Timlin, D. M. *Trans. Faraday Soc.* **1971**, *67*, 1376.

(10) Phillips, D. C.; Trotman-Dickenson, A. F. *J. Chem. Soc. A* **1968**, 1144.

(11) Follmer, D. W.; Pritchard, G. O. *Int. J. Chem. Kinet.* **1974**, *6*, 573.

(12) Holmes, B. E.; Setser, D. W.; Pritchard, G. O. *Int. J. Chem. Kinet.* **1976**, *8*, 215.

(13) Kim, K. C.; Setser, D. W.; Holmes, B. E. *J. Phys. Chem.* **1973**, *77*, 725.

(14) Holmes, B. E.; Paisley, S. D.; Rakestraw, D. J.; King, E. E. *Int. J. Chem. Kinet.* **1986**, *18*, 639.

(15) Hippler, H.; Troe, J.; Wendelken, H. J. *J. Chem. Phys.* **1983**, *78*, 6709.

(16) Joshi, R. M. *J. Macromol. Sci.-Chem.* **1974**, *A8*, 861.

(17) Kolesov, V. P.; Ivanov, L. S.; Skurstov, S. M. *Russ. J. Phys. Chem.* **1975,** *45*, 303.

(18) Pamidimukkala, K. M.; Rogers, D.; Skinner, G. B. *J. Phys. Chem. Ref. Data* **1982**, *77*, 5877.

(19) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Phys. Chem.* **1990**, *93*, 1187.

(20) Rodgers, A. S. In *Fluorine-Containing Free Radicals: Kinetics and Dynamics of Reactions*; Root, J. W., Ed.; ACS Symposium Series No. 66; American Chemical Society: Washington, DC, 1978; pp 269−313.

(21) Rayez, M.; Rayez, J.; Sawersyn, J. *J. Phys. Chem*. **1994**, *98*, 11342.

(22) Martell, J. M.; Boyd, R. J.; Shi, Z. *J. Phys. Chem*. **1993**, *97*, 7208.

(23) Durig, J. R.; Guirgis, G. A.; Li, Y. S. *J. Chem. Phys.* **1981**, *74*, 5946.

(24) Nanair, H.; Guirgis, G. A.; Durig, J. R. *Spectrochim. Acta* **1993**, *49A*, 2039.

(25) Pace, E. L.; Plaush, A. C.; Samuelson, H. V. *Spectrochim. Acta* **1966**, *22*, 993.

(26) Durig, J. R.; Godbey, S. E.; Sullivan, J. F. *J. Chem. Phys.* **1984**, *80*, 5983.

(27) Stolivik, R.; Bakker, P. *J. Mol. Struct.* **1991**, *244*, 27.

(28) Burger, H.; Pawelke, G. *Spectrochim. Acta* **1979**, *35A*, 517, 525.

(29) Cadman, P.; Kirk, A. W.; Trotman-Dickenson, A. F. *J. Chem. Soc., Faraday Trans. 1* **1975**, *72*, 996.

(30) Holmes, B. E.; Setser, D. W. *J. Phys. Chem*. **1978**, *82*, 2461.