Threshold Energy and Unimolecular Rate Constant for Elimination of HF from Chemically Activated $CF_3CF_2CH_3$: Effect of the CF_3 Substituent on the α-Carbon

J. Bridget McDoniel[†] **and Bert E. Holmes***

Department of Chemistry, Lyon College, Batesville, Arkansas 72501

Received: October 3, 1996; In Final Form: December 16, 1996[⊗]

Methyl and CF_3CF_2 radicals were combined to form chemically activated $CF_3CF_2CH_3$ with 104 kcal/mol of internal energy, and the experimental rate constant for unimolecular 1,2-dehydrofluorination was 4.5×10^5 s^{-1}. Fitting the calculated rate constant for HF elimination from RRKM theory to the experimental value provided a threshold energy, E_o, of 68.5 kcal/mol. Comparing this threshold energy to those for CF_2HCH_3, $CH_3CF_2CH_3$, CF_2ClCH_3, and CF_3CH_3 shows that replacing the α-H of CF_2HCH_3 with CH_3 lowered the E_o by 7 kcal/mol and replacing with CF_3, Cl, or F raises the E_o about 8 kcal/mol. The CF_3 substituent, an electron acceptor, increased the E_o by an amount nearly equal to that with F and Cl substituents, suggesting that halogen substituents exert a similar inductive effect at the α-carbon that loses electron density as the transition state forms. These proposals will be compared to recent calculations of the carbon's atomic charges in the reactant and transition state.

Introduction

Chemists have an abiding interest in the atomic and electronic motions occurring as reactants are converted into products. If the movement of electrons is uneven, the atoms acquire partial charges, and elucidating this ionic character is often the first step in understanding the reaction mechanism. A traditional technique to gain insight into the partial charges arising on an atom is the measurement of the effect of substituents on the threshold energy barrier. When substituent effects are analyzed, it is imperative that the change in the electron density, not the absolute charge, be considered because a carbon that retains the same partial charge as the transition state forms will not have its threshold energy affected by substituents. We have used this method[1,2] with chemically activated $CFCl_2CH_3$ and CF_2ClCH_3 and measured unimolecular rate constants for the competitive 1,2-elimination of HF and HCl.

Threshold energies for loss of HF, E_o(HF), and for loss of HCl, E_o(HCl), from CF_2ClCH_3 and $CFCl_2CH_3$ have been determined and compared to those for other chloro- and fluoroalkanes. The data show an increase in the E_o(HF) of 3−7 kcal/mol for replacement of each H on the α-carbon by an F: CH_2FCH_3, 58 kcal/mol;[3,4] CHF_2CH_3, 61 kcal/mol;[5] CF_3CH_3, 68 kcal/mol.[3,6] The α-carbon contains the halogen and the *β*-carbon the hydrogen that are eliminated. Exchanging two Cl's for H's on the α-carbon had an effect upon the E_o(HF) similar to replacement of H's with F's; E_o's for CF_3CH_3, CF_2ClCH_3, and $CFCl_2CH_3$ are, within experimental uncertainty, identical at 68, 69.5, and 68 kcal/mol.[1−4] Therefore, for HF elimination, Cl and F substituents on the α-carbon are equivalent; they increase the E_o.

For HCl elimination, the threshold energies[1,7] for CH_2ClCH_3 and CF_2ClCH_3 are identical at 55 kcal/mol. When two chlorines are present, the E_o's are 52 and 54 kcal/mol for $CHCl_2CH_3$ and $CFCl_2CH_3$, respectively.[2,7] In both mono- and dichlorinated systems, the α-carbon substituents do not significantly affect the E_o and the small decline in E_o(HCl) with successive Cl substitution might arise from steric repulsion between the bulky Cl's. Steric crowding present in the molecule would be reduced with stretching of the C−Cl bond so that additional chlorines would raise the energy for the reactant more than for the transition state, reducing E_o. When HF is eliminated, Cl substituents contribute similar steric repulsions in the molecule and the transition state, so the E_o is unchanged.

It appears that both Cl and F substituents on the α-carbon raise the barrier for loss of HF by 3−7 kcal/mol per halogen substituent; however, F substituents have negligible effect on the barrier for loss of HCl. To account for these observations, either the transition states for HCl and HF elimination are different with Cl and F exhibiting similar substituent effects or there is a complex interplay of F and Cl substituent effects on a common transition state. The present work with chemically activated $CF_3CF_2CH_3$ was designed to resolve the electronic nature of F and Cl substituents.

Theoretical treatment of the 1,2-dehydrohalogenation reaction[8] found that the change in charge at the α-carbon was different for HCl versus HF loss, supporting the concept of dissimilar transition states; i.e., the α-carbon acquired electron density for HF elimination but lost electron density when HCl was removed. However, several kinetic studies of bimolecular reactions[9−12] have measured rate constants that varied in a manner suggesting that the effect of F and Cl substituents depended upon their number and identity. Halogen substituents are known to both donate and withdraw electron density, often displaying a complicated interaction of these two effects when different types of halogens are present. Examples of reactions that exhibit competition between the dual electronic nature of halogen substituents include atomic chlorine abstracting H from halogenated ethanes[9] and methanes,[10] abstraction of H by OH radicals from haloalkanes,[11] and singlet oxygen addition to fluoroethenes.[12]

Tschuikow-Roux and co-workers[9,10] have examined a series of chloro- and fluoromethanes and -ethanes to determine the effect of chlorine and fluorine substituents on the activation energies for hydrogen abstraction by atomic chlorine. The observed trends are attributed to a combination of inductive and resonance effects. Progressive chlorine or fluorine substitution at the α-carbon of an ethane resulted in a decrease in reactivity at both α- and *β*-carbons as well as a preference for hydrogen

---

[†] Current address: Chemistry Department, University of Texas at Austin, Austin, TX 78741.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S1089-5639(96)03032-0 CCC: $14.00

abstraction on the halogenated carbon.[9] The fluoroethanes were found to have higher activation energies for abstraction of hydrogen than analogous chloroethanes. This was explained by greater repulsive dispersion forces between the fluorine substituent, compared to a chlorine substituent, and the incoming chlorine atom.[10] Repulsive dispersive forces cannot be the sole effect, since this would predict a preference for attack at the least substituted carbon, contrary to observation. The decrease in reactivity may arise from chlorine's and fluorine's inductive effects, which should decrease with increasing distance of the H from the substituent; i.e., the withdrawal of electron density should reduce the likelihood of attack by atomic chlorine. The preference for abstraction of the hydrogen on the more highly substituted carbon is ascribed to a resonance effect. Tschuikow-Roux[10] also found that H abstraction from fluoromethanes is increasingly endothermic, suggestive of an increase in the strength of the C−H bond with increasing fluorine substituents. The converse is true for chloromethanes; as the number of chlorine substituents increases, the loss of H becomes increasingly exothermic, indicative of a weakening of the C−H bond.[13]

Hsu and DeMore[11] investigated the gas-phase abstraction of hydrogen from variously substituted halomethanes by hydroxyl radicals. Successive chlorine substitution caused the rate constant per hydrogen to increase; however, the magnitude of the change decreased with each additional chlorine. For fluorine substitution, the first fluorine resulted in an increase, the second in a slight decrease, and the third in a dramatic decrease in the rate constant per hydrogen.

Moss and Jennings[12] analyzed the effect of fluorine substituents upon the relative rates of singlet oxygen addition to fluoroalkenes. Increasing the number of fluorine substituents close to the double bond caused the reactivity at first to decline and then to increase. They suggested that competition between donation and withdrawal of electron density by the substituents is responsible for this trend; i.e., the inductive effect per fluorine decreases with successive fluorination and the magnitude of the resonance effect per fluorine remains constant.

From an analysis of the trends for these three systems, it is apparent that the interplay of resonance and induction is complex and there is no unified explanation for all observations. Because the effect of Cl and F substituents are complex and the interpretation ambiguous, in this work we will use the CF_3 substituent, which is known to withdraw electron density, to investigate the nature of the transition state for 1,2-elimination of HF. The rate constant for loss of HF from $CF_3CF_2CH_3$ will be measured and matched to rates calculated using RRKM theory to determine the E_o(HF). The threshold energy for CHF_2CH_3[5] will be compared to those for $CF_3CF_2CH_3$, $CH_3CF_2CH_3$,[14] $CClF_2CH_3$,[1] and CF_3CH_3[3,6] to ascertain the effect of replacing the H by the CF_3, CH_3, Cl, and F substituents, respectively, at the α-carbon. These trends should determine whether Cl or F substituents remove or release electron density at the α-carbon by comparison to the effect of an electron-withdrawing substituent, CF_3, and to the effect of a CH_3 substituent, which provides electron density through hyperconjugation. In addition, this will ascertain whether electron density flows to or from the α-carbon as the transition state forms, thus clarifying the polar character at the α-carbon.

The chemically activated $CF_3CF_2CH_3$, containing 104 kcal/mol of internal energy, was formed by photolysis of CF_3CF_2I and CH_3I in the presence of Hg_2I_2. These iodides produce CF_3CF_2 and CH_3 radicals,[15] which combine to form $CF_3CF_2CH_3$* (the * denotes chemical activation). The dominant reaction channels follow.

$$2CF_3CF_2I + Hg_2I_2 \xrightarrow{h\nu} 2CF_3CF_2^{\bullet} + 2HgI_2 \qquad (1a)$$

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

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow CH_3CH_3 \qquad (2)$$

$$CF_3CF_2^{\bullet} + CF_3CF_2^{\bullet} \rightarrow CF_3CF_2CF_2CF_3 \qquad (3)$$

$$CF_3CF_2^{\bullet} + {}^{\bullet}CH_3 \rightarrow CF_3CF_2CH_3^{*} \qquad (4)$$

The radical combinations (reactions 2−4) form chemically activated molecules, and the $CF_3CF_2CH_3$* can eliminate HF (reaction 5a) or, at increased pressures, be stabilized through collision (reaction 5b).

$$CF_3CF_2CH_3^{*} \xrightarrow{k_{HF}} CF_3CF{=}CH_2 + HF \qquad (5a)$$

$$\xrightarrow{k_M[M]} CF_3CF_2CH_3 \qquad (5b)$$

The ratio of the products of reactions 5a and 5b is proportional to the rate constant ratio,[16] $[CF_3CF{=}CH_2]/[CF_3CF_2CH_3] = k_{HF}/k_M[M]$, so that a plot of $[CF_3CF{=}CH_2]/[CF_3CF_2CH_3]$ versus inverse pressure (pressure is equivalent to [M]) should have a zero intercept and, if the strong collision assumption is valid for this system, the slope should be linear when $[CF_3CF{=}CH_2]/[CF_3CF_2CH_3] < 1.0$. The slope of the plot equals k_{HF}/k_M, which is converted to k_{HF} by calculation of k_M using collision theory.

Experimental Section

Chemically activated $CF_3CF_2CH_3$ was prepared by photolysis of mixtures containing 3.0 μmol CH_3I and 6.0 μmol CF_3CF_2I in Pyrex vessels containing small amounts of Hg_2I_2 and ranging in volume from 14.85 to 2115.4 cm^3. Samples were prepared on a grease-free vacuum line using an MKS 270 electronic manometer and photolyzed at room temperature for 10 min with a high-pressure Oriel 6137 mercury lamp, normally resulting in 15% conversion of reactants.

A Shimadzu 14A FID GC with a 20 ft × 1/8 in. stainless steel column of Porapak T was used for analysis. By use of an initial temperature of 80 °C for 5 min followed by temperature programming at 1 °C/min to a final temperature of 165 °C, the elution times (in minutes) were generally as follows: C_2H_6, 16 min; C_4F_{10}, 40 min; $CF_3CF{=}CH_2$, 53 min; $CF_3CF_2CH_3$, 59 min; CF_3CF_2I, 102 min; CH_3I, 125 min. The data were collected and integrated with a Shimadzu Chromatopac CR5A integrator. Products were identified by comparison of GC retention times and mass spectra with commercial samples except for $CF_3CF{=}CH_2$. A sample of $CF_3CF{=}CH_2$ was not available, but it demonstrated the pressure dependence expected for unimolecular decomposition of a chemically activated molecule and its mass spectrum showed $m/e = 114$ (relative abundance = RA = 63, the parent ion), $m/e = 113$ (RA = 21, $C_3F_4H^+$ from loss of H from the parent ion), $m/e = 95$ (RA = 50, $CF_2CFCH_2^+$ an allyl radical ion from loss of F from the parent ion), $m/e = 75$ (RA = 11, $C_3F_2H^+$ from loss of HF from the $CF_2CFCH_2^+$ allyl radical ion), and $m/e = 69$ (RA = 100, CF_3^+).

Direct calibration of the flame-ionization detector was not possible for this system because we lacked an authentic sample of $CF_3CF{=}CH_2$. We have found[17] that response factors for fluorinated propenes/propanes are near 1. For example, calibration factors were 1.009 ± 0.011 for $[CF_3CH{=}CF_2]/[CF_3CH_2CF_3]$, 0.953 ± 0.017 for $[CF_3CH{=}CH_2]/[CF_3CH_2CH_3]$, and 1.070 ± 0.066 for $[CF_3CH{=}CF_2]/[CF_3CH_2CH_3]$. Therefore, a

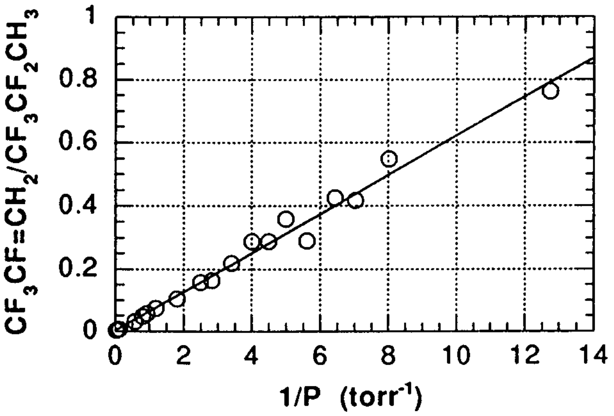

Figure 1. Plot of [$CF_3CF{=}CH_2$]/[$CF_3CF_2CH_3$] versus reciprocal pressure for the four-centered elimination of HF from chemically activated $CF_3CF_2CH_3$. The slope is 0.062 Torr, the intercept is 0.0023, and the correlation coefficient is 0.992.

calibration factor of 1.01 ± 0.04 was obtained for [$CF_3CF{=}CH_2$]/[$CF_3CF_2CH_3$] by averaging these response factors.

Results and Discussion

Measuring yields was straightforward, and only products from reactions 1−5 were detected, indicating secondary reactions were unimportant. In particular we searched for products from the addition of CF_3CF_2 radicals to the $CF_3CF{=}CH_2$, but none were found. Perfluorinated radicals rapidly add to many alkenes,[18] but fluorine substituents deactivate alkenes to radical attack,[19] so the absence of addition products is not surprising. A plot of [$CF_3CF{=}CH_2$]/[$CF_3CF_2CH_3$] versus inverse pressure, Figure 1, had the expected zero intercept with a slope of 0.062 Torr. By calculation of k_M to be 7.2×10^6 Torr^{-1} s^{-1} using temperature independent collision diameters[20,21] of 5.5 (CF_3CF_2I), 4.3 (CH_3I), and 5.0 Å ($CF_3CF_2CH_3$), the k_{HF} converts to 4.5×10^5 s^{-1}.

Our purpose is to determine the E_o(HF) for 1,2-HF elimination from $CF_3CF_2CH_3$ and to compare this to haloalkanes of the formula CXF_2CH_3, where X = H, Cl, F, or CH_3. All the CXF_2CH_3 compounds have been investigated using chemical activation. Often, thermal activation is not useful because HF catalyzes the elimination on hot surfaces. The experimental rate constants in pressure units and reciprocal seconds, the average energy ⟨E⟩, and the E_o's for the CXF_2CH_3 series are in Table 1. The E_o's were determined by matching rate constants calculated using the RRKM theory to the experimental values.

TABLE 1: Experimental Unimolecular Rate Constants in Units of Torr and s^{-1} for 1,2-HF Elimination from CXF_2CH_3 (X = H, Cl, F, CH_3, and CF_3), the Average Energy of the Chemically Activated Molecule, and the Threshold Energy

molecule	k_{HF}/k_M (Torr)	⟨E⟩ (kcal/mol)	k_{HF} (10^8 s^{-1})	E_o (kcal/mol)
CHF_2CH_3	100[a]	95.5	10.0	61[b]
$CClF_2CH_3$	10	101	1.0	69.5[c]
CF_3CH_3	21	102	2.0	68[d]
$CH_3CF_2CH_3$	300	115[e]	30.0	54[e]
$CF_3CF_2CH_3$	0.062	104	0.0045	68.5[f]

[a] The total rate constant was 110 Torr with contributions from 1,1- and 1,2-HF elimination. Based on the 1,1- and 1,2-branching ratio for CHF_2CD_3, the rate constants[5] were 100 Torr for 1,2-HF elimination and 10 Torr for 1,1-HF loss from CHF_2CH_3. [b] Reference 5. [c] Reference 1. [d] Reference 6. [e] The $CH_3CF_2CH_3$ was formed by methylene insertion into the C−H bond of CH_3CF_2H (ref 14). [f] This work.

To validate comparisons, the RRKM calculations were based upon uniform models adjusted to a common thermal preexponential factor of (9.5 ± 1) × 10^{12} s^{-1} per reaction path at 800 K. Models previously developed for CHF_2CH_3,[5] $CClF_2CH_3$,[1] and CF_3CH_3[6] had been parametrized to a thermal preexponential factor within the expected limits and were used without modification. Models were developed for $CF_3CF_2CH_3$ and $CH_3CF_2CH_3$. An earlier version[14] for $CH_3CF_2CH_3$, giving a value that was too high for the preexponential factor, was reevaluated because vibrational frequencies for the molecule are now available.[22] Vibrational frequencies have not been reported for $CF_3CF_2CH_3$, so these were estimated from $CH_3CF_2CH_3$,[22,23] $CF_3CF_2CF_3$,[24] and $CF_3CH_2CF_3$.[25,26] For the four-member transition states, the frequencies were assigned from previous models[3−7] with the ring puckering adjusted to produce the desired preexponential factor (see Table 2).

The average energy of the chemically activated species is the enthalpy of reaction at absolute zero plus the thermal energy of the reactants. The enthalpy of formation at 298 K for $CF_3CF_2CH_3$ is not available; it was estimated as −275 kcal/mol from group additivity schemes,[27] and adjustment to 0 K gave −271 kcal/mol. For the methyl radical $\Delta H_f^o(0\ K) = 35.9$ kcal/mol,[28] and for the CF_3CF_2 radical the −213 kcal/mol (298 K) recommended by Rodgers[29] was corrected to −211 kcal/mol at 0 K. The ΔH^o_{rxn} for reaction 4 at 0 K is −98.6 kcal/mol; addition of 4.9 kcal/mol thermal energy for the two radical reactants gives an ⟨E⟩ = 103.5 kcal/mol, which was rounded to 104 kcal/mol. A value exceeding 100 kcal/mol is in accord with a recent ab initio calculation[30] of the bond dissociation energies for a series of fluoroethanes that predicted the increased

TABLE 2: Summary of Experimental Rate Constants and RRKM Models for 1,1,1,2,2-Pentafluoropropane and 2,2-Difluoropropane

	molecule $CF_3CF_2CH_3$	activated complex, elimination of HF	molecule $CH_3CF_2CH_3$	activated complex, elimination of HF
vibrational frequencies, cm^{-1} (degeneracies)	2942 (3)	2925 (2)	2997 (6)	2852 (6)
	1257 (8)	1228 (7)	1437 (6)	1440 (4)
	902 (3)	849 (5)	1235 (3)	1270 (3)
	584 (6)	573 (5)	953 (4)	954 (4)
	380 (3)	380 (3)	779 (1)	789 (2)
	231 (2)	229 (3)	490 (3)	503 (5)
	91 (2)	82 (1)	304 (4)	300 (2)
moment of inertia $I^‡/I$		0.96		1.0
reaction path degeneracy[a]		4		8
preexponential factor,[b] s^{-1}		8.97×10^{12}		8.93×10^{12}
E_o, kcal/mol		68.5		54
⟨E⟩, kcal/mol		104		115
k_a(exptl), s^{-1}		4.5×10^5		3.0×10^9
k_a(calcd), s^{-1}		4.3×10^5		2.8×10^9

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

ionic character in the C−C bond for CY_3CH_3 (Y = halogen) would cause the bond dissociation energy to be 6 kcal/mol higher than for ethane. We examined the thermochemistry for the other CXF_2CH_3 molecules and retained the $\langle E\rangle$ selected by the authors. The calculated rate constant matched the experimental values with E_o(HF) = 54 kcal/mol for $CH_3CF_2CH_3$, and by use of $\langle E\rangle$ = 104 kcal/mol for $CF_3CF_2CH_3$, E_o(HF) = 68.5 kcal/mol (see Tables 1 and 2). Using a lower $\langle E\rangle$ would require a lower E_o. For example, reducing the $\langle E\rangle$ by 5.0 kcal/mol reduced the k_E by a factor of 2.3 while a 2.0 kcal/mol decrease in the threshold energy (from 68 to 66 kcal/mol) raises the k_E by a factor of 2.3.

Comparing the $CF_3CF_2CH_3$ results to data provided in Table 1 shows that an electron-withdrawing substituent, CF_3, has the same effect on E_o(HF) as both Cl and F, but all these substituents are different from CH_3, which is an electron donor. This strongly suggests that F and Cl substituents are electron acceptors when HF is eliminated.

It appears as though complicated substituent effects, observed for Cl and OH abstracting H from haloalkanes[9−11] and for oxygen addition to fluoroalkenes,[12] are not prevalent when HF is eliminated from haloalkanes. Our findings suggest an increase of E_o(HF) with successive halogen substitution. Replacing the first H of CH_2FCH_3 (E_o = 58 kcal/mol)[1] with an F or Cl substituent causes a slight increase in E_o (E_o = 61 for CHF_2CH_3 and 59 kcal/mol for $CHFClCH_3$);[3,14] however, substituting for the second H increases the E_o an additional 7−10 kcal/mol (see Table 1).

Toto, Pritchard, and Kirtman[8] have calculated molecular and transition state atomic charges on the α- and the β-carbons, on the H and the F being eliminated, and on the α-substituents for CHF_2CH_3, CF_3CH_3, and $CClF_2CH_3$. A consistent picture emerges regarding the change in electron density as the transition state forms: the carbons and the departing fluorine acquire electron density (0.07−0.13 e for the carbons and 0.16−0.19 e for the F) but the hydrogen and the halogen substituents lose electron density (0.2 e for the H and 0.08−0.14 e for the substituents). This suggests that release of electron density occurs from the H to the β-carbon and from the substituents to the α-carbon. The α-carbon also feeds electron density to the F that is leaving, but the net effect is an α-carbon that gains electron density. Assuming that substituents exert the same electronic effect on the reactant and on the transition state, electron-withdrawing substituents would be expected to stabilize the additional electron density on the α-carbon of the transition state and to reduce the threshold energy. However, the present findings show that these substituents actually raise the E_o. Because CF_3, F, and Cl substituents increase the E_o, this suggests that the α-carbon loses electron density as the transition state forms. This is consistent with the long-standing view[7,16,31,32] for the 1,2-dehydrohalogenation that F substituents withdraw electron density from an α-carbon that develops a positive charge. However, this view[7,16,31,32] also suggests that α-Cl substituents donate electron density, but our results[1,2] indicate that Cl behaves similarly to CF_3 and F substituents by removing electron density from the α-carbon.

In summary, it appears that the net effect is flow of electron density from the α-carbon during 1,2-HF elimination. The CF_3, Cl, and F substituents probably withdraw electron density from this carbon, thereby destabilizing the transition state and raising the threshold energy barrier. Additional experimental and theoretical work will be needed to test our suggestions about the changes in the electron density at the α-carbon during 1,2-HF elimination and to reproduce the experimental observations of α-carbon substituent effects on the E_o(HF). We are working[17] on the influence of CF_3 and CH_3 substituents at the β-carbon on the E_o(HF). It remains to be determined if the ab initio calculations[8] will agree with the experimental effect of α-carbon substituents upon the threshold energies when HCl is eliminated, and we intend to explore this in the future.

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

References and Notes

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

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

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

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

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

(6) Marcoux, P. J.; Setser, D. W. *J. Phys. Chem.* **1978**, *82*, 97.

(7) Kim, K. C.; Setser, D. W. *J. Phys. Chem.* **l978**, *78*, 2166.

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

(9) Tschuikow-Roux, E.; Faraji, F.; Niedzielski, J. *Int. J. Chem. Kinet.* **1986**, *18*, 513.

(10) Tschuikow-Roux, E.; Yano, T.; Niedzielski, J. *J. Chem. Phys.* **1985**, *82*, 65.

(11) Hsu, K. J.; DeMore, W. B. *J. Phys. Chem.* **1995**, *99*, 11141.

(12) Moss, S. J.; Jennings, K. R. In *Twelfth International Symposium on Combustion*; Kaufman, F., Ed.; The Combustion Institute: Pittsburgh, PA, 1969; p 301.

(13) Tschuikow-Roux, E.; Faraji, F.; Paddison, S.; Jiedzielski, J.; Miyokawa, K. *J. Phys. Chem.* **1988**, *92*, 1488.

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

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

(16) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: New York, 1972.

(17) Ferguson, J. D.; Henderson, H. A.; Holmes, B. E. To be submitted for publication.

(18) Tedder, J. M.; Walton, J. C. *Acc. Chem. Res* **1976**, *9*, 183.

(19) Tedder, J. M., Walton, J. C., Root, J. W., Eds. *ACS Symposium Series*; American Chemical Society: Washington, DC, 1978; Vol. 66.

(20) Hirschfelder, Y. N.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1965.

(21) Chan, S. C.; Rabinovitch, B. S.; Bryant, J. T.; Spicer, L. D.; Fujimato, T.; Lin, J. O.; Pavlou, S. P. *J. Phys. Chem.* **1970**, *74*, 3160.

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

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

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

(25) Burger, H.; Pawelke, G. *Spectrochim. Acta* **1979**, *33A*, 517.

(26) Jenichen, A. *J. Mol. Struct.: THERMOCHEM.* **1988**, *167*, 227.

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

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

(29) 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.

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

(31) Maccoll, A. *Chem. Rev.* **1969**, *33*, 69.

(32) Egger, K. W.; Cocks, A. T. In *The Chemistry of the Carbon-Halogen Bond*; Patai, S., Ed.; John Wiley & Sons: London, 1973; Part 2, Chapter 10.