J. Phys. Chem. A **2004,** *108,* 3745−3755

Recombination versus Disproportionation Reactions of Hydrogen Atoms with $ClCF_2CHF$, ClC_2F_4, BrC_2H_4, BrC_2F_4, and $BrCF_2CFBr$ Radicals and Unimolecular Reactions of the Haloethane Molecules from Recombination

D. W. Setser,* A. A. Muravyov, and R. Rengarajan[†]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

Received: October 8, 2003; In Final Form: February 17, 2004

The reactions of hydrogen atoms with the $ClCF_2CHF$, ClC_2F_4, BrC_2H_4, BrC_2F_4, and $BrCF_2CFBr$ radicals have been studied at room temperature and 1 Torr pressure of Ar by an infrared chemiluminescence technique in a flow reactor. The $H + CF_3CH_2$ recombination reaction was also examined to provide a reference point to earlier experiments from this laboratory. The recombination step generates vibrationally excited molecules that undergo HX(X = Br, Cl, F) elimination at 1 Torr of pressure. The characteristic low vibrational excitation, $\langle f_V(HX) \rangle \approx 0.15$, with a monotonically declining distribution from unimolecular 1,2-HX elimination reactions versus $\langle f_V(HX) \rangle \approx 0.35$ with an inverted distribution from disproportionation, or direct halogen atom abstraction, reactions is used as a diagnostic test for recombination versus disproportionation mechanisms. Upon the basis of the observed HBr vibrational distributions, the $H + BrC_2F_4$ reaction has a small Br atom abstraction component that is superimposed upon the HBr vibrational distribution from unimolecular HBr elimination. The other reactions proceed only by a recombination−elimination mechanism. The multiple reaction channels, including C−Br rupture and 1,1-HX elimination as well as 1,2-HX elimination, of the haloethanes are discussed. The 1,1-HX elimination channel is important for the CF_2XCF_2H and CF_2XCFXH molecules. The $H + PBr_3$ reaction is discussed in an appendix.

Introduction

Recombination and disproportionation are well-established reaction channels for hydrocarbon radicals.[1,2] The disproportionation-to-combination ratios, k_d/k_c, which have been measured for many radicals,[1−7] are on the order of 0.1 to 0.3 for C_2-C_4 radicals and independent of temperature. The k_d/k_c values do depend on the nature of the radicals, as illustrated by the change in k_d/k_c from 0.14 to 0.30 for self-reactions of ethyl[2] and vinyl radicals.[4] The k_d/k_c ratios also have been measured for many pairs of different radicals.[1] The disproportionation reactions of CF_2H radicals are interesting cases because the stability of the CF_2 product aids the transfer of H atoms.[5] For cross-disproportionation reactions of CF_3[6] or CH_3[7] radicals with hydrocarbon radicals, the disproportionation channel can be viewed as the abstraction of hydrogen from a weak C−H bond of the hydrocarbon radical. Our main interest in this report is the reactions of hydrogen atoms with various halogenated ethyl radicals; the disproportionation channel includes halogen atom (X) abstraction as well as hydrogen atom abstraction.

$$
\begin{aligned}
H + CH_2XCH_2 &\xrightarrow{k_c} CH_2XCH_3^* && \text{(a)} \\
&\xrightarrow{k_{dX}} HX + C_2H_4 && \text{(b)} \qquad \text{(I)} \\
&\xrightarrow{k_{dH}} H_2 + C_2H_3X && \text{(c)}
\end{aligned}
$$

The $D(C-H)$ and $D(C-X)$ bond energies for C_2H_4F (and C_2H_4Cl) are 45 (43) and 44 (20) kcal mol^{-1}, respectively. For most reactions involving hydrogen atoms with radicals, the recombination step is the dominant reaction, and we have utilized these recombination reactions to prepare chemically activated $CH_2XCH_3^*$ molecules in a flow reactor.[8−10] The subsequent unimolecular HX elimination reactions were then studied by infrared chemiluminescence of the HX product.

$$CH_3CH_2X^* \rightarrow HX + C_2H_4 \qquad \text{(II)}$$

Although the chemical products from direct halogen atom abstraction (Ib) and unimolecular elimination (II) are the same, the HX(v) vibrational distributions are quite different vide infra, and these distributions can be used as a diagnostic test. The k_d/k_c values quoted in the early studies of H atoms with halocarbon radicals must be examined carefully because the HX product assigned to disproportionation[11] actually may have been produced by reaction II. As judged from the vibrational distributions, the recombination and halogen abstraction reactions by H atoms with NFCl[12] and CH_2CH_2Cl[9] are competitive, and disproportionation channels are not always negligible. Although the k_d/k_c ratios for ethyl and *n*-propyl radicals with hydrogen atoms are very small (∼0.05), other radicals have larger values. In fact, the H + sec-C_4H_9 reaction[13] has a k_d/k_c ratio of 0.66 ± 0.08, which is similar to that for iso-C_3H_7, and the k_d/k_c ratio for tert-C_4H_9 is reported[1] to be 3.7. The reactions of H atoms with CH_3O and CH_2OH seem to favor disproportionation.[14] In the present work, we wish to report an investigation of the reactions of H atoms with five additional haloethyl radicals (CF_2ClCHF, CF_2ClCF_2, CH_2BrCH_2, CF_2BrCF_2, and $CF_2BrCFBr$). The C_2F_4Cl radical was chosen for comparison to C_2H_4Cl, and the C_2H_4Br and C_2F_4Br radicals were selected to complete the series of F-, Cl-, and Br-containing ethyl radicals.[8,9] Reactions (Ia) release ∼100 kcal mol^{-1} of vibrational energy to the haloethane molecules, and they will undergo unimolecular decomposition at 1 Torr of pressure. In addition

---

* Corresponding author. E-mail: setserdw@ksu.edu.

[†] Present address: Quest International, 5115 Sedge Boulevard, Hoffman Estates, Illinois 60192.

10.1021/jp031144d CCC: \$27.50

to 1,2-HBr, 1,2-HCl, and 1,2-HF elimination, the 1,1-HF elimination process can occur in some cases, and C−Br rupture also must be considered. The recently discovered 1,2-Cl−F exchange reactions[15,16] of vibrationally excited chlorofluoroalkanes may be a complicating factor for the CF_2ClCHF_2 and CF_2ClCH_2F molecules, and this possibility is considered in the Discussion section. The experiments consist of the observation of the infrared chemiluminescence of the HX molecules to distinguish between reactions Ia and Ib. We collected no information about reaction Ic. The H + CF_3CH_2 reaction also was studied to provide a reference point to earlier work.[8,9]

The recombination reactions of H atoms and OH radicals with small radicals have been utilized in our laboratory to generate several chemically activated molecules. The H atom systems usually employed secondary reactions from iodine-containing molecules (e.g., CH_2ClCH_2I and CH_2FCH_2I to generate C_2H_5Cl and C_2H_5F). For some cases, the hydrogen abstraction reactions of OH radicals were used as the source of the radicals. As judged from the product vibrational distributions, the recombination−elimination reactions were dominant for H atoms with CCl_3,[9] CF_3,[8] CF_2Cl,[8,9] CH_2CH_2F,[8] CH_2CF_3,[8] C_2F_5,[8] $CH_2C(O)Cl$,[10] CH_2CH_2OH,[17] $CH_2C(O)OH$,[18] HCO,[19] and CF_3O[20] and for OH radicals with CH_3CO and HCO.[19] Recombination is favored in the reaction of OH with NH_2,[21] but the reactions of O atoms with ethyl, *n*-propyl, and *i*-propyl radicals mainly proceed by direct abstraction, as judged by the OH vibrational distribution.[22] Although the available data are neither extensive nor systematically acquired to answer this question, F and Cl atoms seem mainly to react with hydrocarbon radicals by recombination.[1,23−26] Because recombination and disproportionation channels both have zero, or nearly zero, activation energy, the variation in k_d/k_c values apparently reflects subtle changes in potential energy surfaces that, when treated by transition-state theory,[7c] can lead to different preexponential factors. These disproportionation reactions have similarities to hydrogen atom abstraction reactions that have small, or even negative, activation energies.[27−29]

For reactions of haloethyl radicals, an additional complication is the nature of the CH_2XCH_2 radical as X changes from F to Cl to Br. In particular, the question of the “bridged” structure[30−32] versus the classical radical structure may be important. The role of the bridged structure, which seems to become more important as X becomes heavier, also varies with the substitution of H by F atoms, and electronic structure considerations of the haloethyl radicals may provide some explanation for the disproportionation reactions of these radicals with H atoms or other radicals.

Experimental Methods

These experiments were conducted in the same linear, 40-cm-i.d. flow reactor that previously was employed to study unimolecular reactions of molecules activated by the recombination of radicals with H atoms.[8−10,17−20] The haloethyl radicals were generated by adding the iodine-containing precursor molecule to a flow of H atoms in Ar carrier gas at room temperature. The H atoms were generated by a microwave (2450 MHz, 60 W) discharge in a 1% H_2 in Ar flow through a quartz tube. Several previous measurements have shown that the dissociation of H_2 is ∼50% in this apparatus. The precursor reagent, also diluted in Ar, was added to the reactor via a four-arm showerhead assembly that was placed ∼40 cm downstream from the entrance of the H/H_2 flow into the reactor. The infrared emission from the reactor was viewed through a 3-cm-diameter NaCl window by a Fourier transform spectrometer equipped with a liquid-N_2-cooled InSb detector. The spectrometer was flushed continually with CO_2-free dry air. The center of the observation window was 2.5 cm downstream from the reagent inlet jets, which corresponds to a reaction time of ∼0.2 ms before observation for the maximum flow velocity (120 m/s) of the Ar carrier gas. The reaction time could be lengthened by reducing the flow velocity with a throttling valve placed at the end of the linear flow reactor. The [H] is fully mixed with the Ar carrier during the transient time from the H_2 discharge to the reaction zone. However, the precursor reagent concentration is not fully homogeneous, even though the showerhead assembly was designed to enhance the mixing of the reagent with the Ar carrier gas.

The resolved vibrational−rotational emission spectra from HF, HCl, or HBr, which were acquired at 1−2-cm^{-1} resolution, were subsequently corrected for the wavelength response of the detection system and converted to relative vibrational populations. A representative spectrum from the H + CF_2BrCF_2I reaction is shown in Figure 1; the vibrational−rotational lines are identified by the levels in the upper states. The heights of several P- and R-branch lines of a given vibrational band were divided by the Einstein coefficients of each rotational line to obtain relative vibrational−rotational populations. Because the rotational distributions in 0.5−1.0 Torr of Ar are 298 K Boltzmann, the population in a given rotational level can be scaled to the overall relative vibrational population. For the lowest possible Ar pressure and the shortest reaction time, weak emission from high rotational levels ($J \geq 10$) of HF can be observed from some reactions.[8,20] In the experiments to be reported here, the HF channel was not of particular interest, and no attempt was made to search for a high rotational level component remaining from the nascent rotational distribution. Because we wish to compare relative concentrations of HF to HBr and HF to HCl, it is important to have reliable Einstein coefficients. The rotationless Einstein coefficients for the $\Delta v = -1$ transition of $v = 1-4$ are 194, 334, 423, and 458 s^{-1} for HF,[36] 40.2, 70.0, 89.7, and 99.7 s^{-1} for HCl,[36] and 7.2, 12.8, 16.6, and 18.9 s^{-1} for HBr.[37] The Einstein coefficients for HF and HCl are based on computations using the best available experimental dipole functions, and these Einstein coefficients are very reliable for a wide range of v and J.[36] The Einstein coefficients for HBr were calculated in the same way, but the dipole function[38] is less well defined and these coefficients have greater uncertainty especially for $v = 3$ and 4. Because of the smaller Einstein coefficients, the emission from HBr is weaker than from HCl or HF; however, the detector is more sensitive at smaller wavenumbers, which provides some compensation for the smaller Einstein coefficients. Because HBr elimination is the main pathway for C_2H_5Br, CHF_2CF_2Br, and $CHFBrCF_2Br$ decomposition, the spectra (Figure 1) were adequate for analysis.

The ICF_2CF_2Br, $ICFBrCF_2Br$, ICF_2CF_2Cl, $ICHFCF_2Cl$, and ICH_2CF_3 reagents were purchased from commercial suppliers. We synthesized ICH_2CH_2Br by the Simpson procedure[39] in our laboratory. All samples were degassed and transferred to storage vessels on the vacuum line. Except for ICH_2CH_2Br and $CF_2BrCFBrI$, the reagents were metered from 10-L storage vessels to the flow reactor as a dilute (10%) gas mixture in Ar. The melting point of CH_2BrCH_2I is 32 °C, and the Ar flow was passed over the liquid sample maintained at a constant temperature of ∼50 °C. $CF_2BrCFBrI$ also was added to the reactor by passing Ar over the heated liquid sample. The flow rates of CH_2BrCH_2I and CF_2BrCF_2I were determined by the loss in weight of the liquid samples for a fixed time. The concentrations of H_2, gaseous reagents, and Ar were determined from their

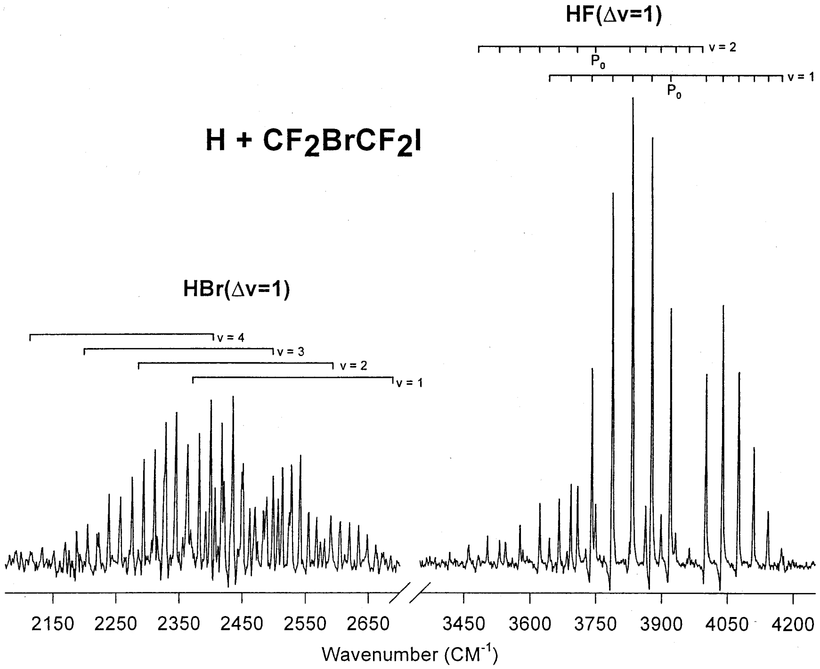

Figure 1. Representative emission spectrum from the H + CF_2BrCF_2I reaction. The HF and HBr spectra have not been adjusted for the response of the detector, which increases in sensitivity by a factor of 2.2 from the 1−0 band of HF to the 1−0 band of HBr. The rotational lines are labeled by the rotational levels of the upper state.

TABLE 1: Thermochemistry[a]

	reaction	$\langle E \rangle$[c]	unimolecular channel	E_o[b]	ΔH^o_o[b]	$\langle E_{av} \rangle$[b]
(1)	H + $CHFCF_2Cl$	104[d]	HCl + $CHFCF_2$	60[h]	30	74
	→ CH_2FCF_2Cl		HF + CHFCFCl	69[h]	24	80
(2)	H + CF_2CF_2Cl	105[d]	HCl + C_2F_4	60[h]	36	69
	→ CHF_2CF_2Cl		HF + CF_2CFCl	69[h]	30	75
			HF + $CFCF_2Cl$	~65	~60	~45
(3)	H + CH_2CH_2Br	104[e]	HBr + C_2H_4	52[j]	17	87
	→ CH_3CH_2Br		Br + C_2H_5	69[g]	69	35
(4)	H + CF_2CF_2Br	103[f]	HBr + C_2F_4	54[j]	34	69
	→ CHF_2CF_2Br		HF + $CFCF_2Br$	~62	~57	~45
			HF + CF_2CFBr	66−68[h]	26	77
			Br + C_2F_4H	68[g]	68	35
(5)	H + $CFBrCF_2Br$	103[f]	HBr + CF_2CFBr	54[j]	~25	~78
	→ $CHFBrCF_2Br$		HBr + $CFCF_2Br$	58−60	~53	~50
			HF + CFBrCFBr	66−68[h]		
			HF + $CBrCF_2Br$	?		
			Br + $CHFCF_2Br$ (or $CHFBrCF_2$)	~66[g]	~66	~37

[a] All entries are in units of kcal mol^{-1}. [b] E_o, ΔH^o_o and $\langle E_{av} \rangle$ are the threshold energies, the enthalpies of reaction, and the available energy for each unimolecular channel, respectively. [c] $\langle E \rangle = D^o_o(C-H) + E_a + \langle E_{thermal} \rangle \approx D^o_o(C-H) + {}^3/_2RT + \langle E_{vib}(R) \rangle$ because $E_a \approx 0$ kcal mol^{-1}. $\langle E_{vib} \rangle$ was taken to be 3.0 kcal mol^{-1}. These values have a ±2−3 kcal mol^{-1} uncertainty. [d] Taken from ref 41. [e] Assumed to be equal to $D(H-CH_2CH_2Cl)$; ref 44. [f] Assumed to be equal to $D(H-CHFCF_2Cl)$; ref 41. [g] References 42 and 43; $D(Br-CHFCF_2Br)$ seems lower than $D(Br-C_2H_5)$; see ref 46. [h] Assigned by analogy to thermal activation studies of C_2F_5H and CF_3CH_2F and chemical activation studies of CH_3CF_2Cl and CH_3CFCl_2; see the text and refs 47−52. [i] See text. [j] References 53 and 54 and the text.

flow rates and the total pressure in the reactors. Flow rates were measured by calibrated flow meters.

Results

A. Thermochemistry. Before presenting the experimental results, a summary of the thermochemistry of reactions 1−5 is presented in Table 1. The thermochemistry of reaction 6

$$H + CH_2CF_3 \rightarrow CH_3CF_3 \rightarrow HF + CH_2CF_2 \qquad (6)$$

can be taken from ref 8, which gives the total vibrational energy, $\langle E \rangle$, as 109 kcal mol^{-1}, the unimolecular threshold energy, E_o, as 68 kcal mol^{-1}, and the total available energy for the products, $\langle E_{av} \rangle = \langle E \rangle - \Delta H^o_o$, as 79 kcal mol^{-1}. The CH_3CF_3 unimolecular reaction has been treated by ab initio electronic structural calculations,[40] which provide insight into the transition-state model for 1,2-HF elimination.

The $D(H-CF_2CF_2Cl)$ and $D(H-CFHCF_2Cl)$ values were taken from ab initio calculations.[41] These values are 2−3 kcal mol^{-1} lower than the $D(H-CF_2CF_3)$ and $D(H-CHFCF_3)$ values.[42,43] $\langle E(CHF_2CF_2Br) \rangle$ and $\langle E(CHFBrCF_2Br) \rangle$ were both assigned as 103 kcal mol^{-1} by analogy to reactions 1 and 2. The $D(C-H)$ value for CH_3CH_2Br was taken to be the same as the recently reported[44] value for $D(H-CH_2CH_2Cl) = 100$ kcal mol^{-1}. The $D(Br-C)$ values are equivalent to the threshold energies for the bromine atom dissociation reactions; the $D(Br-C_2H_5)$[43] and $D(Br-CF_2CHF_2)$[45] values are 68−69 kcal mol^{-1}. The C−Br dissociation energy for $CHFBrCF_2Br$ seems to be lower, and we selected 66 kcal mol^{-1} from an ab initio calculation.[46]

The activation energies for HF elimination for all fluoroethanes have been measured[47] in shock-tube experiments, and the E_o values for CF_3CHF_2 and CF_3CH_2F are in the range of 70−72 kcal mol^{-1}. The replacement of one F atom in the CF_3 group by a Cl atom may lower the HF-elimination threshold energy,[48,49] and we have selected 69 kcal mol^{-1} for 1,2-HF elimination in reactions 1 and 2.

The threshold energies for HF and HCl elimination were assigned as 68 ± 2 and 55 ± 2 kcal mol^{-1} by Holmes and co-workers[48,49] from chemical activation studies of CH_3CFCl_2 and CH_3CClF_2. Upon the basis of this analogy, the difference in threshold energies for HF and HCl elimination for reactions 1 and 2 should be ≥10 kcal mol^{-1}, and HCl elimination should be the dominant unimolecular pathway. However, halogen substitution on the CH_3 group tends to raise threshold energies,[47,50] and E_o for HCl elimination for reactions 1 and 2 may be higher than 55 kcal mol^{-1}. In anticipation of the experimental ratios of HF/HCl from reactions 1 and 2, we have increased the E_o for HCl elimination to 60 kcal mol^{-1}. The 1,1-HF elimination channel becomes important when two F atoms are on the carbon atom containing the H atom.[51,52] This is a consequence of the stability of the singlet CF_3CF carbene, which lowers the enthalpy (and E_o(1,1-HX)) of the reaction. For CHF_2CH_3 and $CHCl_2CH_3$, the threshold energies for the 1,1-HX channels were ~2 kcal mol^{-1} higher than for the 1,2-HX elimination channels.[51,52] However, for CF_3CF_2H and CF_2ClCF_2H, the threshold energy for 1,1-HF elimination may be similar to or even lower than that for 1,2-HF elimination because the replacement of H atoms by F atoms in the CH_3 group raises the threshold energy for 1,2-HX elimination and lowers the threshold energy for 1,1-HF elimination. In anticipation of the experimental results, we selected E_o(1,1-HF) for CF_2ClCF_2H to be 5 kcal mol^{-1} higher than E_o(1,2-HCl) but lower than E_o(1,2-HF).

The threshold energy for HBr elimination[53,54] from C_2H_5Br seems to be reliably established as 52 kcal mol^{-1}. The competing Br + C_2H_5 dissociation channel has a 17 kcal mol^{-1} higher threshold energy. Chemical activation studies[54] show that HBr elimination is the main reaction pathway for C_2H_5Br molecules with an excitation energy of ~100 kcal mol^{-1}.

Fluorine substitution generally raises the E_o(HF) values for fluoroethanes.[47] The results are not quantitative, but E_o(HCl) for CH_2FCH_2Cl is higher than for CH_3CH_2Cl.[50] However, the effect of fluorine substitution on E_o(HCl) was much smaller for CH_3CF_2Cl and CH_3CFCl_2. It seems that E_o(1,2-HBr) for CF_2BrCHF_2 and $CF_2BrCHFBr$ should be higher than for CH_3CH_2Br, and we have estimated 54 kcal mol^{-1} in Table 1. The E_o(1,1-HBr) for reaction 5 is expected to be 4−6 kcal mol^{-1} higher than E_o(1,2-HBr) elimination. The E_o(1,2-HF) values from CF_2BrCHF_2 and $CF_2BrCHFBr$ were assumed to be slightly lower than for CF_2ClCHF_2 and CF_2ClCH_2F. Upon the basis of these estimates, the C−Br rupture channel should become competitive with 1,2-HF elimination for CF_2BrCF_2H and $CF_2BrCFBrH$ because the threshold energies appear to be similar and the transition state for HF elimination has the smaller entropy of activation. The CO_2-laser excitation experiments with bromofluoroethanes[46,55] certainly show evidence for the importance of C−Br rupture, although the level of vibrational excitation in the laser-pumping experiments generally cannot be specified.

The available energy, $\langle E_{av} \rangle$, released to the products can be calculated, $\langle E \rangle - \Delta H^o_o$, if the enthalpy of the reaction[43] is known. The available energy for C_2H_5Br is only about 5 kcal mol^{-1} less than for C_2H_5Cl or C_2H_5F formed by H + CH_2CH_2X. The reactions giving C_2F_4 or C_2F_3X release ~20−15 kcal mol^{-1} less energy than those reactions giving C_2H_4. The enthalpies of formation for CF_2ClCFH_2 (−169.0 kcal mol^{-1}) and CF_2ClCF_2H (−215.5 kcal mol^{-1}) from ab initio studies[42b] were used to calculate ΔH^o_o for reactions 1 and 2. The enthalpy of formation of CF_2HCF_2Br (−200 kcal mol^{-1}) was obtained from $\Delta H^o_f(CF_2HCF_2)$[42] and the ($Br-CF_2CF_2H$) bond dissociation energy.[45a] The enthalpy of formation for $CF_2BrCFBrH$ (~ −142 kcal mol^{-1}) was estimated from $\Delta H^o_f(CF_2BrCF_2H)$ using $D(F-CFHCF_2Br) = 115$ and $D(Br-CFHCF_2Br) = 66$ kcal mol^{-1}.

The enthalpies of reaction for the 1,1-HX elimination reactions are difficult to estimate because the enthalpies of formation of the CF_2XCF carbenes are not established. The estimates given for $\langle E_{av} \rangle$ in Table 1 were obtained from the E_o values of 1,1-HF elimination by assuming that the threshold energy for the reverse reactions was 5 kcal mol^{-1}, which was the estimate for CF_3CH + HCl.[56] The $\langle E_{av} \rangle$ values for 1,1-HX elimination are much smaller than for the 1,2-HF elimination reactions. The carbenes are unstable to F or X migration, and additional internal energy is released if the carbene rearranges to the olefin. The estimates for $\langle E_{av} \rangle$ in Table 1 can be compared with those for the C_2F_5H reaction using information from ab initio calculations for $\Delta H^o_f(CF_3CF)$. The singlet state of CF_3CF is the ground state,[57] and the same trend is expected for CF_2ClCF and CF_2BrCF. Ab initio calculations[58,59] suggest that the $\Delta H^o_f(CF_3CF)$ is ~ −120 kcal mol^{-1}. With this value, the enthalpy of reaction for CF_3CF_2H is 78 kcal mol^{-1}, which is higher than the reported[47] activation energy of 71.6 kcal mol^{-1}. Nevertheless, the trend is in the right direction to support our claim of the importance of 1,1-HF elimination reactions of CF_2XCF_2H giving HF + CF_2XCF in competition with 1,2-HF elimination reactions.

B. HX Vibrational Distributions. *B.1. CF_3CH_3(CF_3CH_2I).* The H + CF_3CH_2I reaction was investigated to ensure that the new experiments were consistent with the earlier study of CF_3CH_3.[8] CF_3CH_2I was added to the H/H_2 flow as a 10% mixture in Ar; the HF emission was strong for a reaction time of 0.3 ms, and the analysis of the spectra was straightforward. Data were collected for H_2 concentrations of $(1-5) \times 10^{13}$ molecules cm^{-3} and for CF_3CH_2I concentrations of $(0.3-12) \times 10^{13}$ molecules cm^{-3}. The HF(v) distributions were independent of the reagent concentrations in these ranges. The average distribution was P_1-P_4 = 49:33:15:5 for HF(v) molecules with a 298 K Boltzmann rotational distribution ($J \leq 6$). This distribution can be compared to the earlier results[8] of P_1-P_4 = 53:32:12:3. The lower P_1 component for the current data is a consequence of the neglect of the small contribution from high rotational levels, $J \geq 8$, to the $v = 1$ population in the present analysis. We conclude that the data from the two studies are in satisfactory agreement, and we can proceed to reactions 1−5 with confidence.

The HF($v = 0$) component of the distribution for the CF_3CH_3 reaction has been established by laser-gain measurements, and the experimental P_0 agrees with the value obtained by extrapolation from a linear surprisal analysis.[8] The HF(v) distribution from CF_3CH_3 together with the distribution from the CH_3CH_2F reaction (Table 4) provides a reference for HF vibrational distributions for 1,2-HF elimination. On the basis of these two examples and our confidence in the P_0 values,[8] $\langle f_V(HF) \rangle = 0.14 \pm 0.02$ can be assigned for 1,2-HF elimination.

B.2. CF_2ClCH_2F ($CF_2ClCHFI$). $CF_2ClCHFI$ was added to the reactor as a 10% mixture in Ar for a reaction time of 0.3 ms. Emission spectra were acquired for H_2 concentrations of $(0.9-3.2) \times 10^{13}$ molecules cm^{-3} and $CF_2ClCHFI$ concentrations of $(0.8-1.8) \times 10^{13}$ molecules cm^{-3}. The HCl and HF emission spectra were both observed, and the analysis was straightforward since the rotational distributions were 298 K Boltzmann. The average distributions from 13 spectra are P_1-P_5 = 36:29:20:11:4 for HCl and P_1-P_4 = 50:31:14:5 for HF. Each vibrational component is based on the peak heights of four to five individual P- and R-branch rotational lines, except for the HCl($v = 5$) population for which only the 5P(0), 5P(1), and 5P(2) lines were observed. The uncertainties in the individual components of the HCl(v) distribution from different spectra are illustrated by the results from experiments shown in Table 2, which have average uncertainties of about ±6%. These results and those to be shown in graphical form for reaction 2 are consistent with previous studies,[8,9,20] which established that HCl(v) relaxation was negligible for $[H] \leq (2.5-3.0) \times 10^{13}$ molecules cm^{-3}. The HCl(v) and HF(v) relative populations were independent of the reagent concentra-

TABLE 2: Vibrational Distributions of HCl from Reaction 1

concentration of [H][a]	HCl vibrational distribution				
	P_1	P_2	P_3	P_4	P_5
1.9×10^{13}	36.5	27.7	20.2	10.9	4.7
2.0×10^{13}	33.4	29.6	20.6	12.4	4.0
2.4×10^{13}	35.7	31.5	18.7	9.9	4.3
2.8×10^{13}	35.1	30.4	20.2	9.8	4.4
2.9×10^{13}	37.3	26.1	19.8	12.5	4.3
2.9×10^{13}	35.2	28.4	20.2	12.1	4.1
3.3×10^{13}	37.2	29.8	19.2	9.0	4.8
3.8×10^{13}	33.2	29.9	21.7	10.3	4.9

[a] In units of molecule cm^{-3}; the $CF_2ClCHFI$ concentration was between 1.0×10^{13} and 1.89×10^{13} molecules cm^{-3}. [b] The HCl(v = 5) component is based on just three vibrational−rotational lines: 5P(0), 5P(1), and 5P(2).

TABLE 3: HX(v) Vibrational Distributions[a]

molecule	HX	P_0	P_1	P_2	P_3	P_4	P_5	$\langle f_V(HX) \rangle$
(1) CF_2ClCFH_2	HCl		36	29	20	11[b]	4	
		34	24	19	13	7	3	0.16
	HF		50	31	14	5	trace	
		41	29	19	8	2		0.14
(2) CF_2ClCF_2H	HCl		52	30	13	5		
		43	30	17	7	3		0.12
	HF		85	12	3	trace		
		62	31	5	2	trace		0.071[b]
(3) C_2H_5Br	HBr		46	37	13	4		
		39	28	22	8	3		0.089
(4) CF_2BrCF_2H	HBr		33	38	22	7	trace	
		25	25	29	16	5		0.18
	HF		85	12	3	trace		
		62	31	5	2	trace		0.068[b]
(5) $CF_2BrCHFBr$[c]	HBr		51	29	16	4		
		41	30	17	9	3		0.095

[a] The second line shows the renormalized distributions with P_0 assigned a value of 1.4 P_1 for the 1,2-elimination reactions and 2.0 P_1 for the 1,1-elimination reactions. The P_0(HBr) value for reaction 4 was assigned as $P_0(HBr) = P_1(HBr)$; see the text. [b] The $\langle f_V(HX) \rangle$ values are based on the total available energy given in Table 1 for 1,2-HX elimination. Because 1,1-HF elimination, rather than 1,2-HF elimination, is dominant for CF_2ClCF_2H and CF_2BrCF_2H, the true $\langle f_V(HF) \rangle$ could be higher than listed. [c] The HF product was negligible; see the text.

tions, and the average distributions from these experiments are listed in Table 3 as nascent distributions. Very weak emission from HF(v = 5) could be observed in spectra with a high signal-to-noise ratio, but the v = 5 population is too low to assign. A comparison of the relative HF and HCl emission intensities shows that the HCl channel is dominant and that the ratio is HCl(v = 1−5)/HF(v = 1−4) = 3.4 ± 0.3.

The HF(v = 1−4) and HCl(v = 1−5) distributions from reaction 1 appear to be characteristic of 1,2-HX elimination from haloethanes, as judged by comparison to distributions from CH_3CH_2F, CH_3CF_3, $CH_3C(O)Cl$, and CH_3CH_2Cl, in Table 4. Thus, we can conclude that the degree of direct Cl atom abstraction from the CF_2ClCHF radical must be minor relative to the recombination−elimination pathway.

B.3. CF_2ClCF_2H (CF_2ClCF_2I). A 10% mixture of CF_2ClCF_2I in Ar was added to the flow reactor for a reaction time of 0.3 ms. The CF_2ClCF_2I concentration was varied from 0.2×10^{13} to 2.5×10^{13} molecules cm^{-3}, and the H_2 concentration was varied from 0.5×10^{13} to 2.7×10^{13} molecules cm^{-3}. Emission was observed from both HCl(v = 1−4) and HF(v = 1−4). Emission probably exists from HCl(v = 5), but it was too weak to be included in the analysis. Some typical distributions are plotted versus [CF_2ClCF_2I] and [H] in Figure 2. The HCl(v) distributions in Figure 2 show no dependence on CF_2ClCF_2I concentration. The HCl(v) distributions for the [H] = 2.7×10^{13} experiments show a slight loss of population from v ≥ 2. Based upon analysis of 8 spectra with [H] ≤ 1.7×10^{13} molecules cm^{-3}, the average distributions (with the statistical uncertainties) are P_1–P_4 = 52 ± 2.0:30 ± 1.3:13 ± 0.6:5 ± 0.2 for HCl and P_1–P_3 = 85 ± 2:12 ± 1:3 ± 0.5 for HF. The relative HCl and HF emission intensities gave an average HCl(v = 1−4)/HF(v = 1−3) ratio of 1.3 ± 0.2 from CF_2ClCF_2H.

TABLE 4: Characteristic HF and HCl Vibrational Distributions from Elimination Reactions

molecule	$\langle E_{av} \rangle$[a]	P_0	P_1	P_2	P_3	P_4	P_5	P_6	$\langle f_V(HX) \rangle$[a]
CH_3CH_2F[b]	91	37.2	25.6	19.4	11.8	4.3	1.7		0.15
CF_3CH_3[b]	79	43.0	30.2	18.2	6.8	1.7			0.13
CH_3CH_2Cl[b,d]	88	28.8	24.2	18.6	13.0	8.3	4.7	2.4	0.16
CH_3CH_2Cl[c]	64	29.9	27.3	20.3	15.4	7.1			0.18
$CH_3C(O)Cl$[b]	85	36.4	24.9	20.3	12.4	6.0			0.12
CF_3OH	116	32.0	33.0	21.0	13.0	7.0	4.0	trace	0.14
CF_3CF_2H[b,e]	67[e]	68.0	26.6	4.5	0.8	0.1			0.064[e]

[a] In kcal mol^{-1} units for 1,2-HX elimination. The distributions were taken from refs 8−10 and 20. [b] Molecule activated by the recombination of haloethyl radicals with H atoms. [c] Molecule activated by the recombination of Cl atoms with ethyl radicals. [d] This distribution for HCl elimination was estimated by the deconvolution of the Cl atom abstraction component from the experimental distribution of the H + CH_2ClCH_2 reaction. [e] The unimolecular reaction probably is 1,1-HF elimination, for which the energy available to the HF + CF_3CF product is ~45 kcal mol^{-1}. $\langle f_V(HF) \rangle$ would increase to ~0.10 for the thermochemistry of 1,1-HF elimination.

The HCl(v) distribution from CF_2ClCF_2H, P_1–P_5 = 52:30:13:5:trace, is consistent with that expected for 1,2-HCl elimination. This HCl(v) distribution provides no support for direct Cl atom abstraction from CF_2ClCF_2. The HF(v) distribution, P_1–P_3 = 85:12:3, is more heavily weighted toward HF(v = 1) than a typical 1,2-HF elimination reaction and, it closely resembles the HF(v) distribution from C_2F_5H shown in Table 4. In both cases, the HF(v) distribution could be the sum from both 1,1-HF and 1,2-HF elimination. The reduced HCl/HF ratio, relative to CF_2ClCFH_2, suggests that the E_o for 1,1-HF elimination is significantly lower than for 1,2-HF elimination from CF_2ClCFH_2. The greater importance of 1,1-HF elimination could arise from a higher E_o for 1,2-HF elimination for CF_2ClCF_2H than for CF_2ClCFH_2, as well as a reduced E_o for 1,1-HF elimination from CF_2ClCF_2H. A lower E_o for 1,1-HF elimination is consistent with the expected thermochemistry for the singlet states of CF_3CF vs CF_3CH.[57−59]

B-4.C_2H_5Br (CH_2BrCH_2I). Because reactions giving HBr have not been studied in this particular reactor, 30 spectra were acquired and analyzed for different operating conditions and two different preparations of CH_2BrCH_2I. The CH_2BrCH_2I was metered to the reactor by flowing Ar over the liquid sample heated to 50 °C. Experiments were done for [H_2] = 0.3−4.5 × 10^{13} molecules cm^{-3} and [CH_2BrCH_2I] ≈ 6 ± 2 × 10^{13} molecules cm^{-3} with an Ar pressure of 1 Torr and a reaction time of 0.3−0.4 ms. The [CH_2BrCH_2I] are only estimates, because they were measured from weight loss of the sample after several spectra were collected. Because the sensitivity of the detector increases in the HBr emission range, 2700−2250 cm^{-1}, relative to the response for the HCl and HF spectra, the HBr emission was moderately strong. However, several of the emission lines are overlapped and only selected P- and R-branch lines from each v level could be used to obtain the vibrational distribution. The v = 4 component is based on only 3−4 P-branch lines and the P_4 component has considerable uncertainty.

The HBr spectra are somewhat surprising in that the v = 1 and 2 bands are much stronger than the v = 3 and 4 bands,

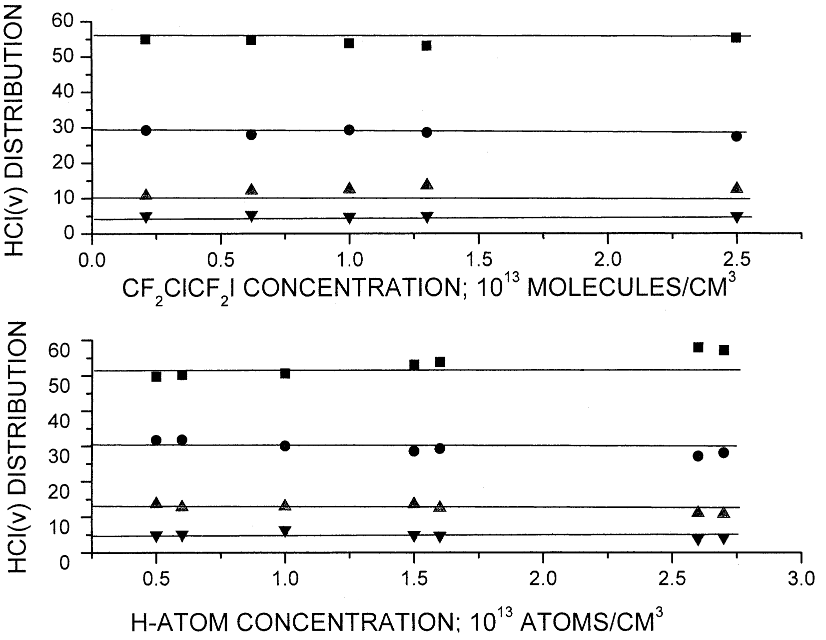

Figure 2. Plot of HCl(v) distributions (■, $v = 1$; ●, $v = 2$; ▲, $v = 3$; ▼, $v = 4$) from various experiments with the H + CF_2ClCF_2I reaction vs the CF_2ClCF_2I and H atom concentrations. For the CF_2ClCF_2I plot, [H] was 1.6 × 10^{13} atoms cm^{-3}. For the H atom plot, [CF_2ClCF_2I] was (1.0 ± 0.2) × 10^{13} molecules cm^{-1}.

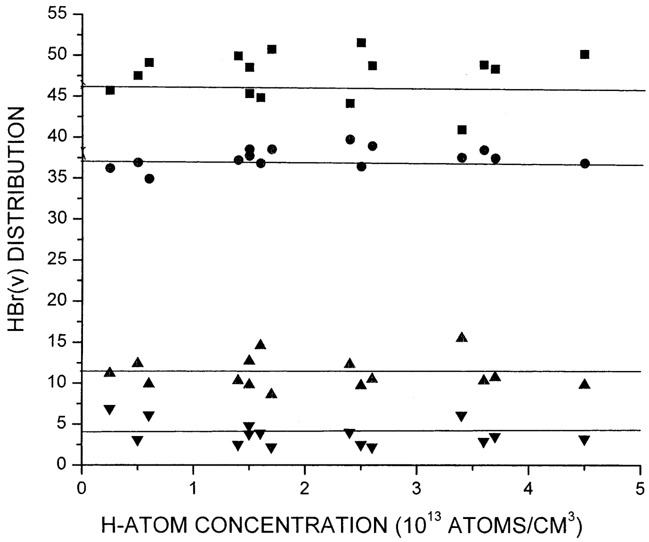

Figure 3. Plot of the HBr(v) distributions vs H atom concentrations for the H + CH_2BrCH_2I reaction (■, $v = 1$; ●, $v = 2$; ▲, $v = 3$; ▼, $v = 4$). The CH_2Br-CH_2I concentration was approximately constant for the experiments. The lines represent the choice for the best overall distribution.

even though the sensitivity of the detector increases by a factor of 2 from the R-branch of $v = 1$ to the P-branch of $v = 4$. However, this trend was true for all spectra and no evidence was found for fast relaxation of $v = 3$. Based upon results from our much earlier study[37] of the H + Br_2 reaction, the most important cause of vibrational relaxation of HBr(v) is the [H]. Several of the HBr(v) distributions are plotted vs [H] in Figure 3. There is no systematic evidence for significant vibrational relaxation for experiments with [H] below 3 × 10^{13} molecules cm^{-3}, although the ratio of P_1/P_2 has more scatter, without a systematic dependence on [H], than would be expected from the quality of the spectra. The best overall HBr(v) distribution selected from the data of Figure 3 is P_1–P_4 = 46:37:13:4. Contrary to expectations based on the H + CH_2ClCH_2 or CH_2FCH_2 reactions, the HBr distribution does not extend to levels beyond $v = 4$, even though HBr($v = 4$) corresponds only to $f_V = 0.33$. The decline in the HBr($v = 3$) population, relative to HBr($v = 2$), somewhat resembles the trend in the HF(v) distribution from CF_3CH_3; see Table 4.

As an additional check on vibrational relaxation of the HBr(v) distribution in this reactor, experiments were done with H + PBr_3 reaction; see the appendix. Because the emission is from a primary reaction and since PBr_3 is commercially available, experiments at low [H] were more convenient. Those results are consistent with little or no relaxation for [H] ≤2 × 10^{13} molecules cm^{-3}.

In principle, the primary reaction with CH_2BrCH_2I could include Br atom abstraction as well as I atom abstraction. The thermochemical limit would be HBr($v = 2$) for Br abstraction. In previous studies[9] with CCl_3Br, CF_2ClBr and CH_2ClCH_2Br only HBr($v = 1$) could be observed from direct Br atom abstraction by the primary reaction. If Br abstraction from CH_2BrCH_2I was important, the HBr(v) distribution should change with [H], since the component from the H + CH_2BrCH_2 reaction would be second-order in [H], and the primary abstraction would be first-order. The I atom abstraction rate constant[60] for CH_3CH_2I at 298 K is 1.0 × 10^{-11} cm^3 molecule^{-1} s^{-1}, and the Br atom abstraction rate constant is ≈20 times smaller.[61] Thus, the observed HBr emission seems to be associated only with reaction 3. The only caveat for the experiments is the higher than desirable concentration of CH_2BrCH_2I. Although it should not be extensive, some relaxation of $v = 3$ and 4 may have occurred. However, this degree of relaxation cannot alter the conclusion that the H + CH_2BrCH_2 reaction mainly proceeds by an addition–elimination mechanism.

B-5.CF_2BrCF_2H (CF_2BrCF_2I). A gaseous mixture of 10% CF_2BrCF_2I was added to the flow reactor. The total pressure was 1 Torr, the reaction time was 0.3–0.4 ms, the [H] was varied from 0.5 to 4.5 × 10^{13} molecules cm^{-3} and the [CF_2BrCF_2I] range was 0.5–3.0 × 10^{13} molecules cm^{-3}. Emission spectra were recorded from both HF and HBr for 20 experiments. The HBr spectra are very different in appearance from the spectra of reaction 3 with emission from $v = 3$ being strong and that from $v = 1$ being relatively weak, as illustrated in Figure 1.

The HF spectra were easy to analyze because most of the emission was from $v = 1$. The average HF(v) distribution was $P_{1-}P_4 = 85{:}12{:}3{:}$trace, this distribution is very similar to those from CF_2ClCF_2H and CF_3CF_2H. The implication is that 1,1-HF elimination is responsible for the HF(v) distribution in all three cases.

The HBr emission was strong except for the experiments with $[H] = 0.5 \times 10^{13}$ molecules cm^3. Relative populations were assigned for $v = 1-4$ and weak emission was also observed from $v = 5$. The HBr(v) distribution showed no dependence on [CF_2BrCF_2I] concentration; however, the relative populations in $v = 1$ and $v = 2$ may have a very weak dependence on [H]. The average HBr(v) distribution from 13 experiments with $[H] \leq 2.5 \times 10^{13}$ cm^{-3} was $P_{1-}P_4 = 33 \pm 2{:}38 \pm 2{:}22 \pm 1{:}7 \pm 1$ with a trace from $v = 5$. If the $[H] = 0.5 \times 10^{13}$ molecules cm^{-3} results (4 experiments) are considered alone, the distribution is $P_{1-}P_4 = 32{:}38{:}23{:}9$ with ±10% uncertainty in each component. The H + C_2F_4Br reaction does seem to give a HBr(v) distribution that has a slight inversion for $v = 2$.

The average ratio of HBr ($v = 1-4$)/HF($v = 1-4$) was 5.3 ± 1.0 from spectra obtained for $[H] = 1.5-3.5 \times 10^{13}$ molecule cm^{-3}. Some of the HF spectra had poor line shapes and this may contribute to the uncertainty of the ratio. The $[H] = 0.5 \times 10^{13}$ molecules cm^{-3} data were not included in the calculation of this ratio because of the noise in the HBr spectra.

B-6.$CF_2BrCFBrH$ ($CF_2BrCFBrI$). Because of the limited sample, only three experiments were done with $CF_2BrCFBrI$. The vapor pressure is low and Ar was passed over the liquid sample to obtain a concentration of 1.6×10^{13} molecules cm^{-3} for $[H] = (2-4) \times 10^{13}$ molecule cm^{-3} and a reaction time of 0.3 ms. The HBr emission was strong and the HBr distribution was $P_{1-}P_4 = 51{:}29{:}16{:}4$. For these conditions, the HF emission was essentially absent. If the time and concentrations were doubled, very weak HF emission from $v = 1$ could be observed, but the HBr emission was still more than 100 times more intense than the HF emission. The virtual absence of HF elimination is consistent with 1,2-HBr elimination and perhaps a small 1,1-HBr elimination component being the important unimolecular reactions, because these E_o values are lower than those for HF elimination from the $CF_2BrCFBrH$ molecule.

A new observation for an experiment with l.7 ms reaction time was emission from Br($^2P_{1/2-}{}^2P_{3/2}$) at 3685 cm^{-1}. The excited Br atom probably is formed by vibrational-to-electronic excitation with HBr($v = 2$).[37] The increase in reaction time and the HBr(v) concentration enables the Br* to be observed. The observation suggests that dissociation of $CF_2BrCFBrH$ to Br and CF_2CFBrH or CF_2BrCFH may be competitive with HBr elimination. The increase in reaction time and the HBr(v) concentration enables Br* to be observed.

Discussion

A. Disproportionation vs Recombination for Reactions 1−5. The principal objective of this work was to search for other examples besides the H + CH_2ClCH_2 reaction that had a disproportionation (or halogen atom abstraction) component. Our criterion was the HX vibrational distributions, which are sharply inverted with $\langle f_V(HX) \approx 0.35$ for direct, bimolecular, halogen atom abstraction reactions and monotonically declining with $\langle f_V(HX) \approx 0.15$ for 1,2-HX unimolecular elimination reactions. A recent combined ab initio electronic-structure plus quasi-classical trajectory treatment[62] for the unimolecular CH_3CH_2F reaction confirms the dynamical model previously proposed[8,17,20] to explain the energy disposal pattern of 1,2-HX elimination reactions. This calculation[62] provides support for the claim of a rather generic HX(v) distribution from unimolecular 1,2-HX elimination reactions. Based upon the less extended HF(v) distributions from CF_3CF_2H and the two molecules investigated here, CF_2ClCF_2H and CF_2BrCF_2H, which correspond to a 2-fold lower $\langle f_V(XH)\rangle$ relative to 1,2-HF elimination, as well as the thermochemical arguments regarding CF_3CF, we suggest that 1,1-HF elimination is the dominant process for these reactions. Of course, if the $\langle E_{av}\rangle$ for 1,1-HF elimination is used, then the $\langle f_V(HF)\rangle$ values would increase.

To calculate the average vibrational energy released to HX, $\langle f_V(HX)\rangle$, the P_0 components of the distribution must be assigned. We have used the trends of the more completely studied reactions in Table 4, which suggest $P_0 = 1.4\ P_1$ for 1,2-HX elimination processes and $P_0 = 2.0\ P_1$ for 1,1-HF elimination reactions. Estimating the P_0 for HBr(v) from H + CF_2BrCF_2 is more difficult because both abstraction and addition−elimination probably occur. In this case we assumed $P_0{=}P_1$. The $\langle f_V(HX)\rangle$ values are given in the last column of Table 4 for the $\langle E_{av}\rangle$ corresponding to 1,2-HX elimination. The $\langle f_V(HX)\rangle$ values are more sensitive to the estimate made for P_0(HX) and to the uncertainty in $\langle E_{av}\rangle$ than to the uncertainties in the measured distributions. The $\langle f_V(HF)\rangle$ values for reactions 2 and 4 listed in Table 3 would increase by approximately a factor of 3 if the $\langle E_{av}\rangle$ for 1,1-HF elimination were used.

Of the 5 reactions studied, only the HBr(v) distribution from H + CF_2BrCF_2 suggests the existence of a measurable (≥15%) component for abstraction. Without more reliable examples of the distributions from HBr elimination and Br abstraction reactions, we will not attempt to estimate a branching fraction for abstraction. The H + C_2H_4Cl and H + C_2F_4Br systems have, at least, one property in common which may explain their propensity to abstraction; the $D(Br{-}C_2F_4)$[35] and $D(Cl{-}C_2H_4)$[33,34] are both approximately 20 kcal mol^{-1}. Both radicals have classical nonbridged structures, although the Cl atom can shuttle between the two carbon centers of C_2H_4Cl at room temperature.[32,34]

Based upon the small $D(Br{-}C_2H_4)$ value,[32] ≈ 8.4 ± 2.2 kcal mol^{-1}, we had anticipated that the H + C_2H_4Br reaction would have an abstraction component. However, the HBr(v) distribution from reaction 3 suggest that this is not the case. A possible explanation for the lack of abstraction is the nonclassical, symmetrically bridged structure of the C_2H_4Br radical, which results in a delocalization of the unpaired electron[32] that could aid the recombination step. The low bond-dissociation energy implies that C_2H_4Br is not thermally stable at 300 K. Although an energy barrier to dissociation could exist, this seems unlikely.[33,34] The reason that we can observe the recombination reaction between H atoms and C_2H_4Br at 300 K is the low pressure of Ar and the short reaction time in the reactor. The rate of the unimolecular dissociation of C_2H_4Br will be limited by collisional activation, i.e., the unimolecular dissociation reaction is far into the falloff regime.

The H + $CH_2C(O)Cl$ reaction mainly proceeds by recombination, even though $D(Cl{-}C(O)CH_2)$[10] is very similar to $D(Cl{-}C_2H_4)$. This difference could be related to the delocalization of the unpaired electron over the $CH_2C(O)Cl$ structure and, thus, BrC_2H_4 and $CH_2C(O)Cl$ reactions may have something in common. Comparison of the half-filled molecular orbitals of CH_3ClCH_2 and $CH_2C(O)Cl$ shows that the electron density on Cl is much higher for CH_2ClCH_2 than for $CH_2C(O)Cl$.[10b] Reports of disproportionation reactions of CH_2ClCH_2 with itself and other radicals are somewhat inconclusive, but both H and Cl transfer does occur.[1]

The C_2F_4Cl and CF_2ClCHF radicals have higher C−Cl bond-dissociation energies (≈ 30 kcal mol^{-1}) than C_2H_4Cl. The calculation[35] for C_2F_4Cl did not find a minimum energy corresponding a stable bridged structure, and these radicals have classical structures. Abstraction of Cl atoms was not found and, in retrospect, would not be expected.

Considering the limited number of experiments, conclusions about the H + $CF_2BrCFBr$ reaction are tentative. Nevertheless, the HBr(v) distribution resembles the one from H + C_2H_4Br rather than the one from H + C_2F_4Br, and recombination followed by HBr elimination seems dominant. The thermochemical estimates given in Table 1 suggest that $D(Br-C_2F_3Br) \approx 10$ kcal mol^{-1}. Additional information about the structure of the $CF_2BrCFBr$ radical, including the possibility of isomerization, would be useful.

B. Competitive Unimolecular Reactions. The recombination step of reactions 1−5 generate vibrationally excited molecules with more than one unimolecular decomposition pathway, and the infrared emission data provide some information about the importance of different channels. The infrared emission from CF_2ClCH_2F is definitive for the importance of 1,2-HF and 1,2-HCl elimination pathways. The ratio of HCl(v≥0)/HF(v ≥ 0) is 3.0 ± 0.3 after adjustment of the measured ratio for the $v = 0$ components. Because the reaction-path degeneracy is 2-fold larger for HF formation, the branching ratio per Cl or F atom is 6. Inspection of RRKM calculations with variable threshold energies for HX elimination reactions of several haloethane molecules[40,48,49,51,64] suggests that the threshold energy for HF elimination must be 6−8 kcal mol^{-1} higher than for HCl elimination to achieve this branching ratio. This difference is approximately 1/2 the difference in $E_o(HF) - E_o(HCl)$ reported by Holmes and co-workers for CF_2ClCH_3 and $CFCl_2CH_3$.[48,49] This analysis must be expanded to include the possibility of Cl−F exchange, which would give the CF_3CH_2Cl molecule.[17,64] The isomerization is 10 kcal mol^{-1} exoergic; however, the only important decomposition pathway for CF_3CH_2Cl is 1,2-HF elimination. Thus, even if ClF exchange competes with 1,2-HCl elimination from CF_2Cl-CH_2F, interpretation of the infrared chemiluminescence data would be basically unchanged.

Interpretation of the results for CF_2ClCF_2H is less straightforward. Adjustment of the HCl(v≥1)/HF(v > 1) = 1.3 ratio for the $v = 0$ components gives a total HCl/HF ratio of ≈0.8, and the reaction probabilities must be approximately equal for the two channels. We already have argued that the HF(v) distribution from reaction 2 is consistent with 1,1-HF elimination, which would have a 2-fold higher reaction path degeneracy than the 1,2-HCl elimination channel. Thus, the branching ratio per Cl and F atom would be ≈1.6 in favor of HCl elimination. This ratio implies that E_o(1,1-HF) is 3−4 kcal mol^{-1} higher than E_0(1,2-HCl) with recognition that the entropy of the transition state for 1,1-HX elimination is larger than for 1,2-HX elimination. A corollary to this conclusion is that E_o(1,2-HF) must be 8−10 kcal mol^{-1} higher than E_o(1,2-HCl), since 1,2-HF elimination is minor. Thus, the substitution of F for H in CF_2ClCFH_2 seems to increase the E_o(1,2-HF). The Cl−F exchange for reaction CF_2ClCHF_2, which has not been studied, would generate CF_3CHFCl. The major unimolecular pathway for CF_3CHFCl is expected[64] to be 1,1-HCl elimination. Indeed, the measured HCl distribution from the CF_2ClCF_2H system may favor P_1(HCl) relative to reaction 1, and a small 1,1-HCl component may exist for reaction 2. The HF distribution does not support 1,2-HF elimination from either CF_3CHClF or from $CF_2Cl-CHF_2$. In conclusion, the major reactions for the CF_2ClCHF_2 system seem to be 1,2-HCl elimination and 1,1-HF elimination from CF_2ClCHF_2.

The competition for the unimolecular decomposition of C_2H_5Br is between HBr elimination and Br atom dissociation. As already mentioned, HBr elimination[53,54] with $E_o = 52$ kcal mol^{-1} is dominant for a vibrational energy of 100 kcal mol^{-1}.

The competitive channels for CF_2BrCF_2H include 1,2-HBr, 1,1-HF and 1,2-HF elimination plus Br atom dissociation. The infrared emission data identify 1,2-HBr and 1,1-HF elimination as the major channels. If we ignore the contribution to HBr formation from Br abstraction from C_2F_4Br, then HBr($v \geq 1$)/HF($v \geq 1$) = 5.3 ± 1.0 becomes ∼2.7 after adjustment for the $v = 0$ components. Because two fluorine atoms can participate, the HBr/HF ratio is ∼5.4 per Br and F atom. E_o(1,1-HF) must be 6−8 kcal mol^{-1} larger than E_o(1,2-HBr), with E_o(1,2-HF) being more than 10 kcal mol^{-1} higher than E_o(1,2-HBr). If E_o(1,2-HBr) is substantially larger than 54 kcal mol^{-1}, then Br atom rupture could be a competitive pathway.

The HBr(v) distribution implies that 1,2-HBr elimination is dominant for reaction 5. However, a small contribution from 1,1-HBr elimination cannot be excluded. The actual E_o(1,2-HBr) value is not known for either reaction 4 or 5. The 1,1-HF elimination process is not competitive because the CF_2BrCBr singlet carbene + HF channel has a larger positive enthalpy of reaction than does the $CFBr_2CF$ + HBr channel. The Br^* emission does identify Br atoms in the H + $CF_2BrCFBrI$ system. If E_o(1,2-HBr) is higher than 54 kcal mol^{-1}, then the Br atom rupture process from $CF_2BrCFBrH$ may be important, although the presence of Br atoms in the reactor from the dissociation of $Br-CF_2CFBr$ cannot be excluded.

Conclusions

Reactions of five haloethyl radicals with H atoms have been studied by the infrared chemiluminescence method in a flow reactor at 298 K. Upon the basis of the HBr vibrational distribution, the H + C_2F_4Br reaction seems to have a disproportionation (direct Br atom abstraction) component in addition to the recombination component. In this sense, the C_2F_4Br reaction resembles the H + C_2H_4Cl reaction. Both reactions have similar C−X bond dissociation energies. To our surprise, the H + C_2H_4Br reaction seems not to have a disproportionation component, even though $D(Br-CH_2CH_2)$ is less than $D(Cl-CH_2CH_2)$. One possible explanation is the difference in structure of C_2H_4Br and C_2H_4Cl. The latter has a classical radical structure, whereas C_2H_4Br has a bridged structure. The other three radicals—CF_2ClCF_2, CF_2ClCFH, and $CF_2BrCFBr$—seem to react only by recombination with H atoms.

The recombination step gives haloethane molecules with ∼104 kcal mol^{-1} of vibrational energy. The unimolecular reactions of CF_2ClCFH_2 seem to be the normal 1,2-HF and 1,2-HCl elimination processes. Upon the basis of thermochemical arguments and upon the similar HF(v) distributions from CF_3CF_2H, CF_2ClCF_2H, and CF_2BrCF_2H, which are less extended than for 1,2-HF elimination reactions, 1,1-HF elimination seems to be important for CF_2ClCF_2H and CF_2BrCF_2H in competition with 1,2-HCl and 1,2-HBr elimination, respectively. This claim suggests that $\Delta H^\circ_f(CF_3CF)$ is lower than current estimates in the literature from ab initio calculations. The CH_3CH_2Br and $CF_2BrCFBrH$ molecules mainly decomposes by 1,2-HBr elimination, although some C−Br rupture also may occur. The recently recognized ClF exchange reaction of vibrationally excited chlorofluoroalkane molecules is included in the discussion.

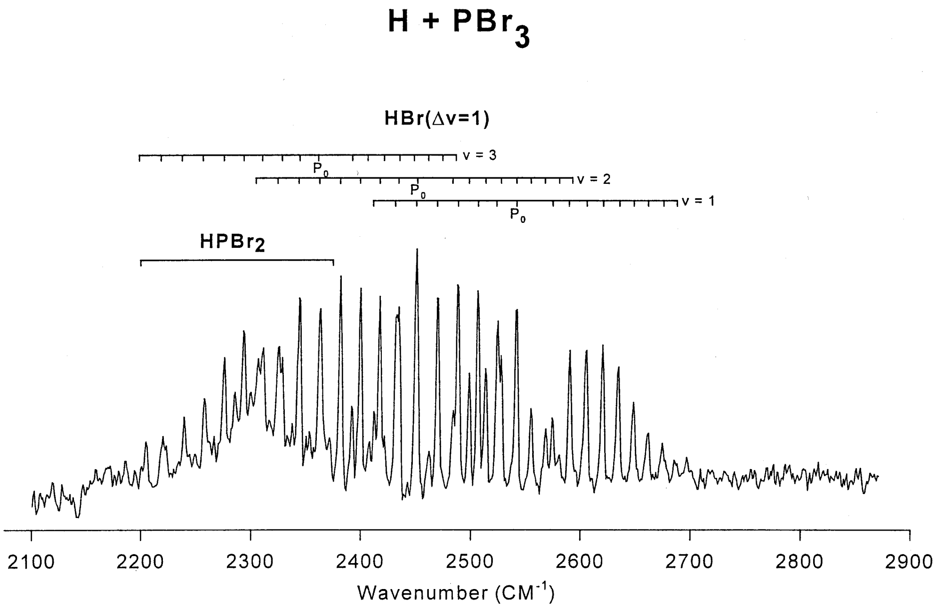

Figure 4. Emission spectrum from the H + PBr_3 reaction. Note the broad emission band at ~2300 cm^{-1} under the HBr emission spectrum.

The reaction of H + PBr_3, which is described in the Appendix, appears to have an addition−elimination and an addition−displacement mechanism. A broad-band emission at ~2300 cm^{-1} may be the P−H stretching emission from $HPBr_2$.

Acknowledgment. We thank Professor Bert Holmes for numerous discussions and for the calculations listed in refs 42b and 64 and Professor Arunan for the electron distribution plots for C_2H_4Cl and $CH_2C(O)Cl$. We also thank Professor E. R. Ritter for communicating the results of his calculations for CF_3-CF and Dr. Wayne Danen for advice on the synthesis of CH_2-ICH_2Br.

Appendix: H + PBr_3 Reaction

As part of a program to characterize the chemistry of the PF radical, we investigated the H + PF_2Cl and PF_2Br reaction systems in the infrared chemiluminescence flow reactor. The objective was to employ the H + PF_2 secondary reaction as a chemical source of the PF($a^1\Delta$) radical. The primary reactions with PF_2Br and PF_2Cl proved to be difficult to study by the infrared emission technique in a flow reactor. The synthesis and gas handling for the required amounts of PF_2Br and PF_2Cl were tedious. Furthermore, the reaction rates giving HBr and HCl seemed to be rather slow; the emissions, which were from v = 1 and 2, were weak and not very reproducible from one experiment to another. In an effort to understand the PF_2Cl and PF_2Br systems better, experiments were done with PBr_3. In an earlier investigation,[37] the rate constant for HBr($v \geq 1$) formation had been reported to be $(1.0 \pm 0.1) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for an observed HBr(v) distribution of P_1-P_3 = 63:24:13 using the infrared chemiluminescence method but with a different and less sensitive apparatus.

The Ar carrier gas flow was passed over the liquid PBr_3 sample, and the flow rate of PBr_3 was deduced from the loss in mass of the liquid sample as $\sim 0.9 \times 10^{13}$ molecules cm^{-3}. The emission intensity was strong for a reaction time of 0.25 ms, and a typical spectrum is shown in Figure 4. The H atom concentration was systematically varied from (0.4 to 1.8) $\times 10^{13}$ atoms cm^{-3}. The HBr(v) distributions from several experiments for [H] $\leq 1.1 \times 10^{13}$ atoms cm^{-3} are shown in Table 5. Within the uncertainty of the data, a dependence of the HBr(v) distribution on [H] for a concentration of less than 1×10^{13} atoms cm^{-3} is not apparent. The average HBr(v) distribution based on experiments with [H] $\leq 1 \times 10^{13}$ molecules cm^{-3} is P_1-P_4 = 52:33:12:3. In the limited study[37] reported in 1980, the observed HBr(v) distribution was P_1-P_3 = 63:24:13. To observe a satisfactory spectrum at that time, relatively high reagent concentrations and long reaction times were required. Because some HBr(v) relaxation was suspected, comparison was made to the H + Br_2 reaction, which gives an inverted nascent HBr(v) distribution. The corrections for the assumed relaxation of the HBr(v) distribution from H + PBr_3 were too large, and the observed steady-state distribution, which resembles the results of Table 5, actually was the better approximation to the nascent distribution.

TABLE 5: HBr(v) Distributions from H + PBr_3[a]

[H] 10^{13} atoms/cm^3	P_1	P_2	P_3	P_4
0.33	53	34	12	2
0.34	53	31	14	2
0.45	46	38	13	3
0.51	48	34	15	3
0.54	49	34	14	3
0.70	53	32	12	3
0.79	57	31	10	2
0.93	57	31	10	2
1.1	54	32	11	3

[a] The concentration of PBr_3 was $\sim 0.9 \times 10^{13}$ molecules cm^{-3}.

In addition to the HBr emission, a broad emission band in the 2100−2425-cm^{-1} region with a maximum at 2300 cm^{-1} is evident in Figure 4. Experiments were done in which the spectrometer was flushed with dry N_2 to ensure that the broad-band emission was not related to residual CO_2 in the CO_2-free dry air that normally was used for flushing. This broad-band emission existed in all of the spectra, and the ratio of the integrated HBr and the broad-band intensities was 1.6 ± 0.3. The P−H stretching modes[66,67] in PH_2F and PH_2Cl are near 2300 cm^{-1}, and those for PHF[68] and PHCl[69,70] are around 2260 cm^{-1}. The 2300-cm^{-1} band in Figure 4 is tentatively assigned as the P−H stretching mode emission of $HPBr_2$.

The observation of the $H{-}PBr_2$ emission and the monotonically declining $HBr(v)$ distribution is suggestive of a reaction mechanism involving H atom addition to the phosphorus atom followed by a competition between Br atom displacement and HBr elimination.

$$\mathrm{H + PBr_3 \rightarrow H{-}PBr_3 \rightarrow HBr}(v)\mathrm{ + PBr_2}$$
$$\rightarrow \mathrm{H{-}PBr_2 + Br}$$

The available energy for the HBr pathway is $\sim$33 kcal mol^{-1} based[37] on $D(Br{-}PBr_2) = 63 \pm 2$ kcal mol^{-1}. The displacement reaction is exothermic by $\sim$17 kcal mol^{-1} based upon a generic $D(P{-}H)$ value of $\sim$80 kcal mol^{-1}.

The results from the H + PBr_3 reaction suggest that the H + PF_2Cl and PF_2Br reactions also may proceed by an addition mechanism, which could yield three sets of products, for example, HF + PFBr, HBr + PF_2, or HPF_2 + Br (although the 2300-cm^{-1} emission was never observed). The emission of HF from the H + PF_3 reaction could not be observed in our reactor at room temperature even for long reaction times and high reagent concentrations, and direct abstraction of an F atom from PF_2Cl or PF_2Br is not expected. However, if the reaction proceeds by addition to a phosphorus atom of PF_2Br or PF_2Cl, then subsequent HF formation could occur. Thus, the observation of HF emission from the H + PF_2Br and PF_2Cl systems does not necessarily imply that the H + PF_2 secondary reaction was observed. However, in separate experiments both $PF(X^3\Sigma^-)$ and $PF(a^1\Delta)$ in approximately equal proportions were observed for long (1-ms) reaction periods from H + PF_2Cl using laser-induced fluorescence to monitor PF(X) and PF(a). Further work is required to understand both the kinetics and thermochemistry of the H + PF_2Br and PF_2Cl reaction as well as the H + PCl_3 system.[70,71] In closing, we note that oxygen atoms also react with PH_3 by an addition mechanism.[72]

References and Notes

(1) *CRC Handbook of Bimolecular and Termolecular Gas Reactions*; Kerr, J. A., Ed.; CRC Press: Boca Raton, FL, 1981; Vol. 2, p 80.

(2) Dobis, O.; Benson, S. W. *J. Am. Chem. Soc.* **1990**, *112*, 1023.Dobis, O.; Benson, S. W. *J. Am. Chem. Soc.* **1991**, *113*, 6377.

(3) Friedrichs, G.; Herbon, J. T.; Davidson, D. F.; Hanson, R. V. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5799.

(4) Fahr, A.; Laufer, A. H. *J. Phys. Chem.* **1995**, *99*, 262.

(5) Pritchard, G. O.; Follmer, D. W.; Meleason, M. A.; Shoemaker, D. D.; Perkins, J. C.; Leupp, S. L. *Int. J. Chem. Kinet.* **1992**, *24*, 735.

(6) (a) Smith, S. R.; Holmes, B. E. *Int. J. Chem. Kinet.* **1999**, *31*, 237. (b) Ferguson, J. D.; Holmes, B. E. *Int. J. Chem. Kinet.* **2001**, *33*, 549 and other papers in this series.

(7) (a) Cohen, L. K.; Pritchard, H. O. *Can. J. Chem.* **1985**, *63*, 2374. (b) Benson, S. W. *J. Phys. Chem.* **1985**, *89*, 4366. (c) Mousavipour, S. H.; Homayoon, Z. *J. Phys. Chem. A* **2003**, *107*, 8566.

(8) Arunan, E.; Wategaonkar, S. J.; Setser, D. W. *J. Phys. Chem.* **1991**, *95*, 1539.

(9) Arunan, E.; Rengarajan, R.; Setser, D. W. *Can. J. Chem.* **1994**, *72*, 568.

(10) (a) Srivatsava, A.; Arunan, E.; Manke, G., II; Setser, D. W.; Sumathi, R. *J. Phys. Chem. A* **1998**, *102*, 6412. (b) Private Communication with Professor Arunan, 2003.

(11) (a) Clark, D. T.; Tedder, J. M. *Trans. Faraday Soc.* **1966**, *62*, 393, 405. The overall reaction mechanism for H + CCl_3 assumed by the authors appears to be correct; however, the extent of stabilization of vibrationally excited $CHCl_3$ probably was overestimated. (b) Tedder, J. M.; Walton, J. C. *Prog. Reac. Kinet.* **1967**, *4*, 48. The k_d/k_c ratio of 0.2 quoted for H + CCl_3 seems not to have been reported in ref 11a, and the justification for this ratio is not explained.

(12) (a) Arunan, E.; Liu, C. P.; Setser, D. W.; Gilbert, J. V.; Coombe, R. D. *J. Phys. Chem.* **1994**, *98*, 494. (b) Shamasundar, K. R.; Arunan, E. *J. Phys. Chem. A* **2001**, *105*, 8533.

(13) Lexton, M. J.; Marshall, R. M.; Purnell, H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 663.

(14) Dóbé, S.; Bérces, T.; Temps, F.; Wagner, H. Gg.; Ziemer, H. *J. Phys. Chem.* **1994**, *98*, 9792.

(15) (a) Burgin, M. O.; Heard, G. L.; Martell, J. M.; Holmes, B. E. *J. Phys. Chem. A* **2001**, *105*, 1615. (b) Heard, G. L.; Holmes, B. E. *J. Phys. Chem. A* **2001**, *105*, 1622. (c) Beaver, M. R.; Heard, G. L.; Holmes, B. E. *Tetrahedron Lett.* **2003**, *44*, 9265.

(16) Dolbier, W. R., Jr.; Romelaer, R.; Baker, J. M. *Tetrahedron Lett.* **2002**, *43*, 8075.

(17) Butkovskaya, N. I.; Setser, D. W. *J. Chem. Phys.* **1996**, *105*, 8064.

(18) Butkovskaya, N. I.; Manke, G., II; Setser, D. W. *J. Phys. Chem.* **1995**, *99*, 11115.

(19) Butkovskaya, N. I.; Setser, D. W. *J. Phys. Chem. A* **1998**, *102*, 9715.Butkovskaya, N. I.; Setser, D. W. *J. Phys. Chem. A* **2000**, *104*, 9428.

(20) Rengarajan, R.; Setser, D. W.; DesMarteau, D. D. *J. Phys. Chem.* **1994**, *98*, 10568.

(21) Fagerström, K.; Jodkowski, J. T.; Lund, A.; Ratajczak, E. *Chem. Phys. Lett.* **1995**, *236*, 103.

(22) Lindner, J.; Loomis, R. A.; Klaassen, S. J.; Leone, S. R. *J. Chem. Phys.* **1998**, *108*, 1944.

(23) Sumathi, R.; Nguyen, M. T. *J. Phys. Chem. A* **1998**, *102*, 8150.

(24) Donaldson, D. J.; Watson, D. G.; Sloan, J. J. *Chem. Phys.* **1982**, *68*, 95.

(25) (a) Donaldson, D. I.; Sloan, J. J. *J. Chem. Phys.* **1985**, *82*, 1873. (b) Butovskaya, N. I.; Setser, D. W. Unpublished work that confirms the results of ref 25a for the F + HCO reaction.

(26) Seakins, P. W.; Woodbridge, E. L.; Leone, S. R. *J. Phys. Chem.* **1993**, *97*, 5633.

(27) Chen, Y.; Tschuikow-Roux, E. *J. Phys. Chem.* **1993**, *97*, 3742.

(28) Atadinç. F.; Selçuki, C.; Sari, L.; Aviyente, V. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1797.

(29) Henon, E.; Canneaux, S.; Bohr, F.; Dóbé, S. *Phys. Chem. Chem. Phys.* **2003**, *5*, 333.

(30) Skell, P. S.; Traynham, T. G. *Acc. Chem. Res.* **1984**, *17*, 160.

(31) Engels, B.; Peyerimhoff, S. D.; Skell, P. S. *J. Phys. Chem.* **1990**, *94*, 1267.

(32) Ihee, H.; Zewail, A. H.; Gooddard, W. A., III. *J. Phys. Chem. A* **1999**, *103*, 6638.

(33) Knyazev, V. D.; Kalinovski, I. J.; Slagle, I. R. *J. Phys. Chem. A* **1999**, *103*, 3216.

(34) Braña, P.; Menéndez, B.; Fernández, T.; Sordo, J. A. *Chem. Phys. Lett.* **2000**, *325*, 693.

(35) Ihee, H.; Kua, J.; Goddard, W. A., III; Zewail, A. H. *J. Phys. Chem. A* **2001**, *105*, 3623.

(36) Arunan, E.; Setser, D. W.; Ogilive, J. F. *J. Chem. Phys.* **1992**, *97*, 1734.

(37) Malins, R. J.; Setser, D. W. *J. Chem. Phys.* **1980**, *73*, 5666.

(38) Bernage, P.; Niay, P. *J. Quant. Spectrosc. Radiat. Transfer* **1977**, *18*, 314. Bernage, P.; Niay, P. *J. Quant. Spectrosc. Radiat. Transfer* and erratum **1981**, *25*, 95.

(39) Simpson, M. *Ber.* **1874**, *7*, 130.

(40) Martell, J. M.; Beaton, P. T.; Holmes, B. E. *J. Phys. Chem. A* **2002**, *106*, 8471.

(41) Chandra, A. K.; Uchimaru, T. *J. Phys. Chem. A* **2000**, *104*, 9244.

(42) (a) Zachariah, M. R.; Westmoreland, P. R.; Burgess, D. R., Jr.; Tsang, W.; Melius, C. F. *J. Phys. Chem.* **1996**, *100*, 8737. (b) Holmes, B. E. Private communication. The $\Delta H^o{}_f(CF_2ClCH_2F)$ and $\Delta H^o{}_f(CF_2ClCHF_2)$ values were calculated to be −169.0 and −215.5 mol^{-1} at 298 K. These values are consistent with the $\Delta H^o{}_f$ of the fluoroethyl radicals given in ref 42a for accepted $D(Cl{-}C)$ values.

(43) Kerr, J. A.; Stocker, D. W. In *Handbook of Chemistry and Physics*; Lide, D. R., Jr., Ed.; CRC Press: Boca Raton, FL, 2002; pages 952 to 976; see also section 5 (thermochemistry).

(44) Seetula, J. A. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1933. Seetula, J. A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3069.

(45) (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (b) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B.; Iorish, V. S. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere Publishing Corporation: New York, 1991.

(46) Yokoyama, A.; Yokoyama, K.; Fujisawa, G. *J. Chem. Phys.* **1994**, *101*, 10602.

(47) (a) Millward, G. E.; Tschuikow-Roux, E. *J. Phys. Chem.* **1972**, *76*, 292. (b) Tschuikow-Roux, E.; Millward, G. E.; Quiring, W. J. *J. Phys. Chem.* **1971**, *75*, 3493.

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

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

(50) (a) Rajakumar, B.; Arunan, E. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2897. (b) Rakestraw, D. J.; Holmes, B. E. *J. Phys. Chem.* **1991**, *95*, 3968. The HCl + CF_2CHF product is now interpreted as ClF exchange followed by HCl elimination. (c) Ferguson, H. A.; Ferguson, J. D.; Holmes, B. E. *J. Phys. Chem. A* **1998**, *102*, 5393.

(51) (a) Kim, K. C.; Setser, D. W.; Holmes, B. E. *J. Phys. Chem.* **1973**, *77*, 725. (b) Kim, K. C.; Setser, D. W. *J. Phys. Chem.* **1974**, *78*, 2166. (c) Holmes, B. E.; Setser, D. W.; Pritchard, G. O. *Int. J. Chem. Kinet.* **1976**, *8*, 215.

(52) Difelice, J. J.; Ritter, E. R. *Combust. Sci. Technol.* **1996**, *116*−*117*, 5.

(53) Jung, K.-H.; Kang, S. H.; Ro, U. R.; Tschuikow-Roux, E. *J. Phys. Chem.* **1987**, *91*, 2354.

(54) Johnson, R. L.; Setser, D. W. *J. Phys. Chem.* **1967**, *71*, 4366.

(55) Pushpa, K. K.; Kumar, A.; Vatsa, R. K.; Naik, P. D.; Rao, K. A.; Mittel, J. P.; Parthasarathy, V.; Sarkar, S. K. *Chem. Phys. Lett.* **1995**, *240*, 489. Pushpa, K. K.; Kumar, A.; Vatsa, R. K.; Naik, P. D.; Rao, K. A.; Mittel, J. P.; Parthasarathy, V.; Sarkar, S. K. *Chem. Phys. Lett.* **1996**, *249*, 167.

(56) (a) Holmes, B. E.; Rakestraw, D. J. *J. Phys. Chem.* **1992**, *96*, 2210. (b) The 1,1 elimination of HCl from CF_3CH_2Cl is no longer considered to be a decomposition step because of Cl−F exchange.[12,16] However, the discussion of addition reactions of the carbenes to HX is still relevant.

(57) (a) Garcia, V. M.; Castell, O.; Reguero, M.; Caballol, R. *Mol. Phys.* **1996**, *89*, 1395. (b) O'Gara, J. E.; Dailey, W. P. *J. Am. Chem. Soc.* **1994**, *116*, 12016.

(58) Peterson, S. D.; Francisco, J. S. *J. Phys. Chem. A* **2002**, *106*, 3106.

(59) Ritter, E. R. Private communication.

(60) Yuan, J.; Wells, L.; Marshall, P. *J. Phys. Chem. A* **1997**, *101*, 3542.

(61) Rebbert, R. E.; Lias, S. G. Ausloos, P. *Int. J. Chem. Kinet.* **1973**, *5*, 893.

(62) Sun, I.; Hase, W. L. *J. Phys. Chem. A* in press, 2003.

(63) Nathanson, G. M.; Minton, T. K.; Shane, S. F.; Lee, Y. T. *J. Chem. Phys.* **1989**, *90*, 6157.

(64) Holmes, B. F.; Heard, G. L. Private communication, 2003. Preliminary ab initio calculations suggest that E_o(HCl) is ∼2 kcal mol^{-1} lower than E_o(Cl−F) for CF_2ClCFH_2 but that E_o(HF) is ∼2 kcal mol^{-1} higher than E_o(Cl−F) for CF_3CH_2Cl. The experimental data[50b,65] for CF_3-CH_2Cl show that 1,2-HF elimination is more important than Cl−F exchange (which leads to HCl + $CF_2{=}CHCl$).

(65) Setser, D. W.; Lee, T.-S.; Danen, W. C. *J. Phys. Chem.* **1985**, *89*, 5799. The low fluence and low-temperature experiments show that the 1,2-HF elimination product is more important than Cl−F exchange (which is followed by 1,2-HCl elimination from CF_2ClCH_2F).

(66) Beckers, H.; Bürger, H.; Kuna, R.; Paplewski, M.; Thiel, W. *J. Chem. Phys.* **1994**, *101*, 5585.

(67) Breidung, J.; Thiel, W.; Demaison, J. *Chem. Phys. Lett.* **1997**, *266*, 515.

(68) Schürmann, B. L.; Knowles, D. B.; Hirsch, G.; Buenker, R. J. *Chem. Phys. Lett.* **1988**, *145*, 529.

(69) Baraille, I.; Larrieu, C.; Dargelos, A.; Chaillet, M. *Chem. Phys.* **2003**, *289*, 263.

(70) Bramwell, M. J.; Rodgers, D. M.; McDouall, J. J. W.; Whitehead, J. C. *Chem. Phys. Lett.* **2000**, *331*, 483.

(71) Wickramaaratchi, M. A.; Setser, D. W.; Hildebrandt, B.; Korbitzer, B.; Heydtmann, H. *Chem. Phys.* **1984**, *84*, 105.

(72) Nava, D. F.; Stief, L. J. *J. Phys. Chem.* **1989**, *93*, 4044.