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Unimolecular Reactions of Chemically Activated $CF_2BrCF_2CH_3$ and $CF_2BrCF_2CD_3$: Evidence for 1,2-FBr Interchange

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Vibrationally excited $CF_2BrCF_2CH_3$ and $CF_2BrCF_2CD_3$ molecules were prepared with 96 kcal mol^{-1} energy at room temperature by the recombination of CF_2BrCF_2 and CH_3 (CD_3) radicals. The observed unimolecular reactions are 1,2-BrF interchange to give $CF_3CFBrCH_3$ (CD_3) molecules and 2,3-FH (FD) elimination; the rate constants are 2.2×10^5 (1.5×10^5) s^{-1} and 2.0×10^5 (0.75×10^5) s^{-1}, respectively. The $CF_3CFBrCH_3$ (CD_3) molecules rapidly, relative to the reverse reaction, eliminate HBr or DBr to give the observed product $CF_3CF{=}CH_2$ (CD_2). Density functional theory at the B3PW91/6-311+G(2d,p) level was used to obtain vibrational frequencies and moments of inertia of the molecule and transition states for subsequent calculations of statistical rate constants for $CF_2BrCF_2CH_3$ and $CF_2BrCF_2CD_3$. Matching experimental and calculated rate constants gave threshold energies of 62 and 66 kcal mol^{-1} for 1,2-BrF interchange and 2,3-FH elimination, respectively. The BrF interchange reaction is compared to ClF interchange from $CF_2ClCF_2CH_3$ and $CF_2ClCHFCH_3$.

I. Introduction

The unimolecular interchange of Cl and F atoms located on adjacent carbon atoms in fluorochloroalkanes has been experimentally demonstrated for $CF_2ClCF_2CH_3$,[1−3] $CF_2ClCHFCH_3$,[1] and $CF_2ClCHFC_2H_5$[4] with ~95 kcal mol^{-1} energy. The Cl/F interchange reaction also exists for several vibrationally excited hydrochlorofluoroethanes.[5−7] These interchange reactions are in competition with unimolecular elimination of HCl and HF. In the present study we wish to report the unimolecular interchange of Br and F atoms in the $CF_2BrCF_2CH_3$ molecule activated by recombination of CF_2BrCF_2 and CH_3 radicals. The results for $CF_2BrCF_2CH_3$ were confirmed by experiments with CD_3 radicals to generate $CF_2BrCF_2CD_3$. The interchange reaction generates $CF_3CFBrCH_3$ (CD_3), which rapidly eliminates HBr (DBr), and $CF_3CF{=}CH_2$ (CD_2) is the observed product from the interchange reaction. The 2,3-FH elimination reaction is in competition with the 1,2-FBr reaction. The bromine atom dissociation reaction is not important relative to the other two processes. The $CF_2BrCF_2CH_3$ class of molecules is of some interest for fire-retardant and refrigeration applications.[8]

Experimental rate constants for $CF_2BrCF_2CH_3$ (CD_3) were obtained from plots of the ratio of decomposition (D_i) to collisionally stabilized (S) products vs pressure^{-1}. These rate constants measured for molecules with 96 kcal mol^{-1} energy are compared to RRKM (Rice−Ramsperger−Kassel−Marcus) calculated values that are based on molecular and transition-state models obtained from electronic structure calculations from density functional theory (DFT). We used the B3PW91/6-311+G(2d,p) level for consistency with previous work.[9−12] This methodology has been developed to assign threshold energies for a series of chlorofluoroethanes, -propanes, and -butanes.[1,4,9−11] In the present work threshold energies are assigned for 2,3-FH (FD) elimination and 1,2-FBr interchange; the latter has the lower threshold energy. In the near future[13] we will examine other computational methods and other basis sets for unimolecular reactions of haloalkanes involving a bromine atom.

The Br−F interchange in $CF_2BrCF_2CH_3$ can be contrasted with Cl−F interchange in $CF_2ClCF_2CH_3$.[1−3] Given their similarity and the common occurrence of Cl−F interchange reactions in fluorochloroalkanes, unimolecular Br−F interchange reactions in vibrationally excited bromofluoroalkanes may be generally expected, if the Br and F atoms are on adjacent carbon atoms.

The CF_2BrCF_2 radical was produced by photolysis of CF_2BrCF_2I and CH_3 (CD_3) radicals were produced from photolysis of CH_3I (CD_3I) at room temperature. The photochemistry of CF_2BrCF_2I is of current interest,[14−16] and the experimental methods for these experiments are described in detail.

II. Experimental System and Procedures

The CF_2BrCF_2 radical has a classical structure with $D(\mathrm{Br}{-}C_2F_4) = 20 \pm 4$ kcal mol^{-1}, and the radical is stable to dissociation at room temperature.[14−16] Lee and co-workers[16] showed that photolysis of CF_2BrCF_2I at 308 nm gave CF_2BrCF_2 + $I(^2P_{3/2})$ or $I(^2P_{1/2})$. The excited $I(^2P_{1/2})$ channel was favored (77%) relative to the ground-state (23%) channel. All of the CF_2BrCF_2 radicals associated with the $I(^2P_{1/2})$ pathway were stable, and only 35% of the CF_2BrCF_2 radicals associated with $I(^2P_{3/2})$ formation had enough vibrational energy to dissociate. The authors concluded that 90% of the CF_2BrCF_2 radicals were stable from 308 nm photolysis of CF_2BrCF_2I. In our experiments we photolyzed 2:1 mixtures of CH_3I and CF_2BrCF_2I in Pyrex vessels with a 200 W high-pressure Hg lamp. The effective wavelength range of ≥280 nm corresponds to the long wavelength limit of the n → n* absorption band. The observed products at high pressure from our photolysis experiments are consistent with the expected recombination and disproportion-

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TABLE 1: Mass Spectral Fragmentation Data at 70 eV (*m*/*e*, Relative Abundance (RA), and Assignment)

CF_2BrCF_2Br			$CF_2BrCF_2CF_2CF_2Br$		
m/*e*	RA	assignment	*m*/*e*	RA	assignment
179	100	$C_2F_4{}^{79}Br^+$	131	100	$CF_2{}^{81}Br^+$
181	97	$C_2F_4{}^{81}Br^+$	129	84	$CF_2{}^{79}Br^+$
129	41	$CF_2{}^{79}Br^+$	69	60	$CF_3{}^+$
131	37	$CF_2{}^{81}Br^+$	31	50	CF^+
31	32	CF^+	100	44	$C_2F_4{}^+$
100	24	$C_2F_4{}^+$	279	36	$C_4F_8{}^{79}Br^+$
50	15	$CF_2{}^+$	191	35	$C_3F_4{}^{79}Br^+$

$CF_2BrCF{=}CH_2$			$CF_2BrCF{=}CD_2$		
m/*e*	RA	assignment	*m*/*e*	RA	assignment
95	100	$C_3F_3H_2{}^+$	97	100	$C_3F_3D_2{}^+$
69	45	$CF_3{}^+$	69	41	$CF_3{}^+$
45	17	$C_2FH_2{}^+$	47	17	$C_2FD_2{}^+$
129	16	$CF_2{}^{79}Br^+$	31	11	CF^+
131	15	$CF_2{}^{81}Br^+$	76	6	$C_3F_2D^+$
31	9	CF^+	129	4	$CF_2{}^{79}Br^+$
75	7	$C_3F_2H^+$	131	4	$CF_2{}^{81}Br^+$

$CF_2BrCF_2CH_3$			$CF_2BrCF_2CD_3$		
m/*e*	RA	assignment	*m*/*e*	RA	assignment
65	100	$C_2F_2H_3{}^+$	68	100	$C_2F_2D_3{}^+$
115	60	$C_3F_4H_3{}^+$	118	27	$C_3F_4D_3{}^+$
45	29	$C_2FH_2{}^+$	47	18	$C_2FD_2{}^+$
51	18	CF_2H^+	52	11	CF_2D^+
26	6	$C_2H_2{}^+$	31	9	CF^+
95	6	$C_3F_3H_2{}^+$	131	4	$CF_2{}^{81}Br^+$
44	5	C_2FH^+	129	4	$CF_2{}^{79}Br^+$

ation reactions of CF_2BrCF_2 and CH_3 radicals; the asterisk denotes vibrational excitation.

$$CF_2BrCF_2 + CH_3 \rightarrow CF_2BrCF_2CH_3{}^* \qquad (1a)$$

$$\rightarrow CH_3Br + C_2F_4 \qquad (1b)$$

$$2CF_2BrCF_2 \rightarrow CF_2BrCF_2CF_2CF_2Br^* \qquad (2a)$$

$$\rightarrow CF_2BrCF_2Br + C_2F_4 \qquad (2b)$$

$$2CH_3 \rightarrow C_2H_6{}^* \qquad (3a)$$

The $CF_2BrCF_2CF_2CF_2Br^*$ and $C_2H_6{}^*$ molecules are collisionally stabilized at the pressures of our experiments; however, $CF_2BrCF_2CH_3{}^*$ has two unimolecular reaction pathways that compete with collisional deactivation at reduced pressures.

$$CF_2BrCF_2CH_3{}^* \rightarrow CF_3CFBrCH_3{}^* \qquad (4a)$$

$$\rightarrow CF_2BrCF{=}CH_2 + HF \qquad (4b)$$

$$k_M\,[M] \qquad CF_2BrCF_2CH_3 \qquad (4c)$$

The $CF_3CHFCH_3{}^*$ molecules acquire about 3 kcal mol^{-1} additional energy in the rearrangement (4a), and HBr elimination occurs before stabilization by collision.

$$CF_3CFBrCH_3{}^* \rightarrow CF_3CF{=}CH_2 + HBr \qquad (5)$$

Although calibrations were not done for C_2F_4 or CH_3Br, the apparent yields were consistent with the expected contributions from (1b) and (2b), and no evidence was found for the decomposition of CF_2BrCF_2 from excess vibrational energy from primary photolysis or from secondary photolysis.

Experiments with pressures ranging from 1.0 to 0.025 Torr were done at room temperature in Pyrex vessels with volumes ranging from 34.7 to 2021.0 cm^3 containing between 0.20 and 5.0 μmol of CH_3I or CD_3I and between 0.10 and 2.0 μmol of CF_2BrCF_2I, plus small amounts of mercury and mercury(I) iodide. The photolysis lamp was a high-pressure Oriel 6137 arc lamp operating with a 200 W mercury bulb. The presence of the mercury(I) iodide in the vessels during photolysis aids formation of the methyl and 1-bromo-1,1,2,2-tetrafluoroethyl radicals.[17] Photolysis times between 3 and 25 min gave about 10% conversion of the reactants to products. All of the gas samples were prepared on grease-free vacuum lines, and a MKS 270C signal conditioner was used to measure pressures. The CH_3I and CF_2BrCF_2I were purchased from Aldrich and PCR, respectively; they were transferred to the vacuum line after several freeze−thaw pump cycles.

Identification of the products were based on mass spectral fragmentation patterns from a Shimadzu QP50000 GC/MS analysis; see Table 1. An authentic sample of $CF_3CF{=}CH_2$ was available for confirmation, but CF_2BrCF_2Br, $(CF_2BrCF_2)_2$, $CF_2BrCF_2CH_3$, and $CF_2BrCF{=}CH_2$ and the deuterated analogues were identified by mass spectrometry. A Rtx-5 105 m column with a diameter of 0.25 mm was used in the GC/MS analyses. The temperature program began with a temperature of 30° for 20 min followed by heating at a rate of 2 deg/min until 100 °C was obtained; then the rate was increased by 4 deg/min until a final temperature of 200 °C was reached.

Analysis of the reaction mixtures to obtain ratios of decomposition to stabilization products were conducted on the Shimadzu gas chromatograph GC-14A with a flame ionization detector (FID) and a Shimadzu CR5A Chromatopac Integrator. A Rtx-5, 0.53 mm × 105 m, column was used. The GC-14A oven was programmed to hold a constant column temperature of 35 °C for a period of 20 min; thereafter, the temperature was increased at a rate of 12 deg/min until 190 °C was reached. The temperature of the flame detector housing was 200 °C. The average retention times of the products of interest were as follows: $CF_3CF{=}CH_2$ at 7.8 min; $CF_2BrCF_2CH_3$ at 14.5 min; $CF_2BrCF{=}CH_2$ at 15.2 min; CH_3I at 18.9 min; CF_2BrCF_2Br at

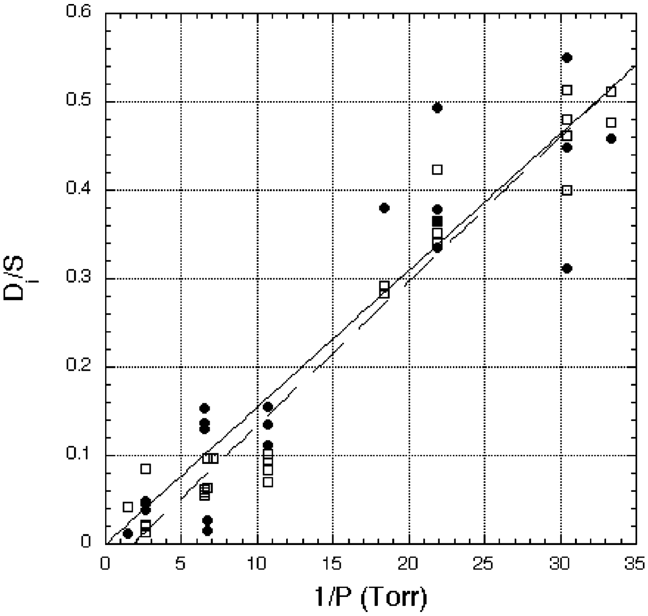

Figure 1. Plots of $CF_2BrCF{=}CH_2/CF_2BrCF_2CH_3$ (□) and $CF_3CF{=}CH_2/CF_2BrCF_2CH_3$ (●) vs pressure^{-1}. The slopes and intercepts for the $CF_2BrCF{=}CH_2$ data are 0.0155 ± 0.0014 Torr and 0.0004 ± 0.02, respectively, and for the $CF_3CF{=}CH_2$ data are 0.0163 ± 0.0007 Torr and −0.029 ± 0.014, respectively.

20.1 min; CF_2BrCF_2I at 31.0 min; $CF_2BrCF_2CF_2CF_2Br$ at 32.3 min. Deuterated products had retention times similar to those of undeuterated products. The retention times for the QP-5000 GC/MS analysis were similar to those just summarized for the Shimadzu GC-14A.

Since samples of $CF_2BrCF{=}CH_2$ and $CF_2BrCF_2CH_3$ were not available, we assumed that the responses of the FID to the product olefins and to $CF_2BrCF_2CH_3$ were the same. This assumption has been tested and confirmed in our laboratory[1,3,4,9−11] for several haloalkane and haloalkene pairs that differ from one another by loss of HCl, HF, or HBr.

III. Experimental Results

The experimental data consist of ratios of $CF_2BrCF{=}CH_2/CF_2BrCF_2CH_3$ and $CF_3CF{=}CH_2/CF_2BrCF_2CH_3$ and the corresponding ratios for the $CF_2BrCF_2CD_3$ system measured at various pressures. These results are summarized in Figure 1 for $CF_2BrCF_2CH_3$ and in Figure 2 for $CF_2BrCF_2CD_3$. The $CF_3CF{=}CH_2$ product is a surrogate for $CF_3CFBrCH_3$, since the latter decomposes by 2,3-BrH elimination at all pressures employed in these experiments. The slopes of these D_i/S plots give unit deactivation rate constants for reactions 4a and 4b, because the data points extend only to $D_i/S \leq 0.6$ for efficient bath gases. The least-squares linear fits to the data points pass close to the origin with correlation coefficients of about 0.95. The slopes of these plots have uncertainties on the order of ±10%.

The four rate constants derived from the slopes of the plots in Figures 1 and 2 are listed in Table 2. The rate constants for 1,2-BrF interchange (0.016 Torr) and 2,3-FH elimination (0.015 Torr) are the same to within experimental uncertainty. Since the kinetic isotope effect is larger for HF/DF elimination than for BrF interchange, the BrF interchange rate constant is 2 times larger than that for 2,3-FD elimination for $CF_2BrCF_2CD_3$. The kinetic isotope effects are 2.80 ± 0.42 and 1.44 ± 0.22 for HF elimination and interchange, respectively. These kinetic isotope effects are in the range expected[3,4,10] for these processes at energies of 96 kcal mol^{-1}. Given the modest experimental uncertainties and the self-consistent kinetic isotope effects, the rate constants of Table 2 should be reliable.

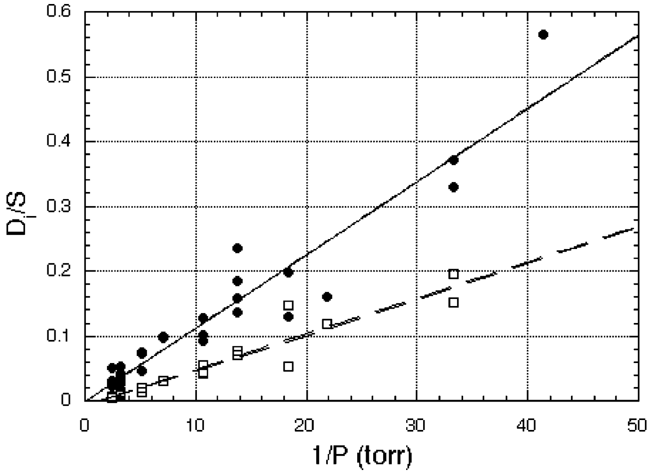

Figure 2. Plots of $CF_2BrCF{=}CD_2/CF_2BrCF_2CD_3$ (□) and $CF_3CF{=}CD_2/CF_2BrCF_2CD_3$ (●) vs pressure^{-1}. The slope and intercepts for the $CF_2CF{=}CD_2$ data are 0.0055 ± 0.0004 Torr and −0.066 ± 0.005, respectively, and for the $CF_3CF{=}CD_2$ data are 0.0113 ± 0.0007 Torr and −0.000008 ± 0.010872, respectively.

The rate constants in Torr units were converted to s^{-1} using the collision constant, k_M, which was calculated using the collision diameters and ϵ/k values given in footnote *a* of Table 2. Since the collision diameters and ϵ/k values have not been measured for $CF_2BrCF_2CH_3$ and CF_2BrCF_2I, they were estimated by considering the probable changes in these values used for $CF_2ClCHFCH_3$ and $CF_2ClCFHI$ and for $CF_2ClCF_2CH_3$ and CF_2ClCF_2I. The conversion to s^{-1} units increases the uncertainty of the experimental rate constants, and we assigned ±25% as the overall uncertainty of the rate constants in s^{-1} units listed in Table 2. This uncertainty also includes the possible error associated with the lack of direct calibration of the GC/FID for the measurements of the $CF_2BrCF_2CH_3$ and $CF_2BrCF{=}CH_2$ products.

IV. Calculated Results

A. Average Energy of $CF_2BrCF_2CH_3$ and $CF_3CFBrCH_3$. The average energy of the $CF_2BrCF_2CH_3$ molecule is mainly determined by the $CF_2BrCF_2{-}CH_3$ bond dissociation energy. Since the $\Delta H°_f(CF_2BrCF_2CH_3)$ and $\Delta H°_f(CF_2BrCF_2)$ are not known with accuracy, we decided to adopt the average energy assigned to $CF_2ClCF_2CH_3$ formed by recombination of CF_2ClCF_2 and CH_3 radicals. This assumption is equivalent to assuming that $D(CH_3{-}CF_2CF_2Cl)$ and $D(CH_3{-}CF_2CF_2Br)$ are the same. In our previous analysis for $CF_2ClCF_2CH_3$, we adopted $\langle E \rangle = 98$ kcal mol^{-1} based upon $\Delta H°_{f,298}(CF_2ClCF_2) = -164.4 \pm 4$ kcal mol^{-1}. This value was derived from a study of the $F + CF_2ClCF_2{-}Cl$ reaction, which employed $D_{298}(CF_2ClCF_2{-}Cl) = 78 \pm 2$ kcal mol^{-1} and $\Delta H°_{f,298}(CF_2ClCF_2Cl) = -212.6$ kcal mol^{-1} from estimations by Rodgers.[20a] Subsequently Buckley and Rodgers[20b] favored $\Delta H°_{f,298}(CF_2ClCF_2Cl) = -215.2 \pm 0.9$ kcal mol^{-1} based upon experimental studies of chlorination of C_2F_4.[20c,d] If −215.2 kcal mol^{-1} for $\Delta H°_{f,298}(C_2F_4Cl_2)$ is used with $D_{298}(CF_2ClCF_2{-}Cl)$ from Foon and Tait,[19] then $\Delta H°_{f,298}(CF_2ClCF_2)$ becomes −166 ± 4 kcal mol^{-1}. Although the uncertainty in $\Delta H°_{f,298}(CF_2ClCF_2)$ is ±4 kcal mol^{-1}, it seems prudent to use −166 kcal mol^{-1}, which lowers $\langle E(CF_2ClCF_2CH_3) \rangle$ to 96 kcal mol^{-1}. The $D_{298}(CF_2ClCF_2{-}Cl)$ value of 78 kcal mol^{-1} is strongly supported by DFT calculations of Ihee and co-workers.[15] Thus, $\langle E(CF_2BrCF_2$-

TABLE 2: Experimental Rate Constants[a,b]

	$CF_2BrCF_2CH_3$		$CF_2BrCF_2CD_3$	
reaction	Torr	s^{-1}	Torr	s^{-1}
BrF interchange	0.016 ± 0.001	$(2.18 \pm 0.54) \times 10^5$	0.011 ± 0.001	$(1.50 \pm 0.37) \times 10^5$
FH elimination	0.015 ± 0.001	$(2.04 \pm 0.51) \times 10^5$	0.0055 ± 0.0004	$(0.75 \pm 0.19) \times 10^5$

[a] Collision diameters (and ϵ/k) values for $CF_2BrCF_2CH_3$, CH_3I, and CF_2BrCF_2I were 5.6 Å (430 K), 4.6 Å (405 K), and 5.4 Å (390 K); $k_M = \pi d^2_{AM}(8kT/\pi\mu_{AM})^{1/2}\Omega^{22}(T^*)$. These choices were based on the values used for the $CF_2ClCHFCH_3$ system.[1] [b] The uncertainty in the rate constants in s^{-1} units was increased to ±25% because of the uncertainty in the collision cross sections.

$CH_3)\rangle = 96$ kcal mol^{-1} was used for the purpose of matching calculated and experimental rate constants. The average energy of $CF_2BrCF_2CD_3$ increases to 96.3 kcal mol^{-1}. The energy of $CF_3CFBrCH_3$ is that of $CF_2BrCF_2CH_3$ plus the enthalpy change of the interchange reaction. According to the DFT calculations, the enthalpy change is -3.3 kcal mol^{-1} and $\langle E(CF_3CFBrCH_3)\rangle$ is 99.3 kcal mol^{-1}.

B. Vibrational Frequencies and Moments of Inertia. We have used density functional theory (DFT) at the B3PW91 level with 6-31G(d′,p′) and 6-311+G(2d,p) basis sets to calculate vibrational frequencies and movements of inertia (from the structures) for fluorochloralkanes and their transition states for HF and HCl elimination and for Cl−F interchange.[1−4,9−12] These calculated results have been tested against experimental structural data, and they have been judged satisfactory as input requirements to calculate rate constants from transition-state theory.[1,9−11] In the present work, we have continued this strategy to obtain vibrational frequencies for $CF_2BrCF_2CH_3$ and the two transition states from B3PW91/6-311+G(2d,p) calculations. In the future[13] we will do a more systematic study of DFT calculations for the C_2H_5Br and C_3H_7Br reactions for which experimental data are available for properties of the molecule and for its unimolecular reaction. Based upon the conclusions of the early work of Toto, Pritchard, and Kirtman,[21] extension of the B3PW91/6-311+G(2d,p) calculations to $CF_2BrCF_2CH_3$ should provide satisfactory estimates for structures and frequencies of the molecule and the two transition states. Identification of transition-state geometries followed the procedure summarized earlier.[2,3,12] The presence of the heavy Br atom may make the calculated threshold energies from the 6-311+G(2d,p) basis set somewhat less reliable than for fluorochloropropanes, although the results below seem quite reasonable. The vibrational frequencies and moments of inertia of the three conformers for the molecule and for the FH transition state were averaged. Two of the molecular conformers actually have the same geometry. The most stable conformer has the Br atom and the CH_3 group in trans positions, but the other conformer is only 0.6 kcal mol^{-1} higher in energy, see Figure 1 in the Supporting Information. The average vibrational frequencies and moments of inertia used for $CF_2BrCF_2CH_3$ and $CF_2BrCF_2CD_3$ and the HF elimination and BrF interchange transition states are listed in a table in the Supporting Information. The structures of the two transition states are shown in Figure 3. All calculations were done with the Gaussian 03 suite of codes.[22]

An alternate mechanism to FBr interchange with subsequent HBr elimination that would form $CF_3CF{=}CH_2$ is 1,3-HBr elimination that forms $CF_2CF_2CH_2$ as a diradical intermediate. We used a variety of DFT methods but could not locate a transition state for 1,3-HBr elimination. While we cannot rule out the existence of the 1,3-pathway, we think it is unlikely for two reasons. First, the F on the central carbon of the $CF_2CF_2CH_2$ diradical could migrate to either of the end carbons forming $CF_3CF{=}CH_2$, which was observed, or $CF_2{=}CFCH_2F$, which was not observed. Second, the H/D kinetic isotope effect for 1,3-HBr/1,3-DBr elimination would probably be close to 3.0, the value observed[3,10,11] for the 1,2-hydrogen halide elimination pathway, rather than the 1.5 measured for $CF_2BrCF_2CH_3$/$CF_2BrCF_2CD_3$.

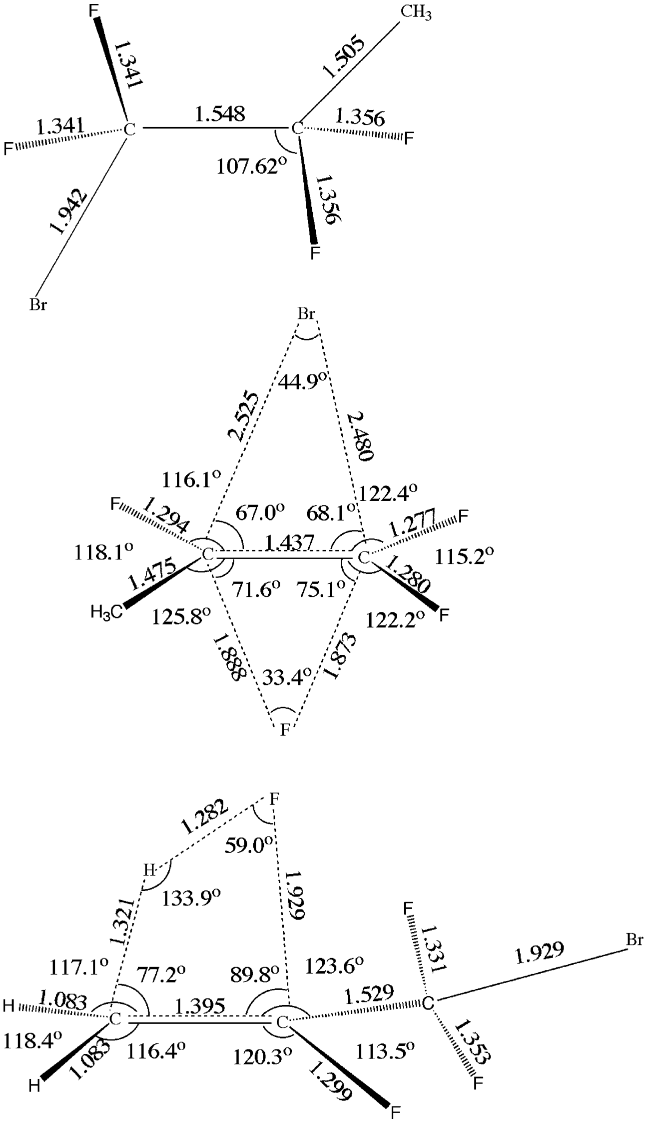

Figure 3. Diagrams of the calculated structures for $CF_2BrCF_2CH_3$, the 1,2-BrF interchange and the 2,3-FH elimination transition states. Note that the C−Br distance in the approximately symmetric bridged transition state has increased from 1.94 Å in the CF_2Br group to 2.52 and 2.48 Å; the C−F distance increased from 1.36 to 1.87 and 1.89 Å. The structure of the 2,3-FH elimination transition state is normal; see ref 10. Carbons 1 and 2 of the interchange transition state are nearly sp^2 hybridized because the angle between the triangular plane defined by the CF_2 and the C−C is 178.7° and the corresponding angle for the triangular plane defined by the $F-C-CH_3$ at C-2 is 177.8°. Carbons 2 and 3 of the HF elimination transition state must have substantial sp^2 character because the angle defined by the CH_2 triangular plane and the C−C bond is 154.7° and the corresponding angle for C-2 is 164.9°.

TABLE 3: Comparison of Calculated and Experimental Rate Constants

molecule	k_{expt} (s^{-1})	k_{calc}[a] (s^{-1})	E_0 (kcal mol^{-1})	preexponential factor[b] (s^{-1})
$CF_2BrCF_2CH_3$				
1,2-BrF	$(2.2 \pm 0.5) \times 10^5$	2.9×10^5	62 ± 2	1.2×10^{13}
2,3-FH	$(2.0 \pm 0.5) \times 10^5$	2.3×10^5	66 ± 2	5.2×10^{13}
$CF_2BrCF_2CD_3$				
1,2-BrF	$(1.5 \pm 0.4) \times 10^5$	1.6×10^5	62 ± 2	1.2×10^{13}
2,3-FD	$(0.75 \pm 0.19) \times 10^5$	0.63×10^5	67 ± 2	4.6×10^{13}
$CF_2ClCF_2CH_3$[c]				
1,2-ClF	$(0.43 \pm 0.06) \times 10^5$	0.47×10^5	66 ± 2	1.1×10^{13}
2,3-FH	$(6.5 \pm 1.0) \times 10^5$	7.0×10^5	64 ± 2	4.1×10^{13}

[a] The calculated values are for $\langle E \rangle = 96.0$ and 96.3 kcal mol^{-1} for $CF_2BrCF_2CH_3$ and $CF_2BrCF_2CD_3$, respectively. [b] In partition function form at 1000 K with inclusion of the reaction degeneracy factors. [c] These experimental and calculated results are described in refs 3 and 1, respectively. The calculated rate constants have been adjusted to $\langle E \rangle = 96$ kcal mol^{-1} for the (2d,p) basis set.

The transition state for 2,3-FH elimination from $CF_2BrCF_2CH_3$ can be compared to that from $CF_2ClCF_2CH_3$.[1] The geometries of the two four-centered rings are nearly identical with $r(C-H) = 1.321$ and 1.315 Å, $r(F-H) = 1.28$ and 1.29 Å, $r(C-F) = 1.93$ and 1.96 Å, and $r(C-C) = 1.39$ and 1.39 Å for $CF_2BrCF_2CH_3$ and $CF_2ClCF_2CH_3$, respectively. The calculated threshold energies, relative to the most stable conformers, for 2,3-FH elimination from $CF_2BrCF_2CH_3$ and $CF_2ClCF_2CH_3$, are 61.6 and 63.8 kcal mol^{-1}, and the overall preexponential factors at 1000 K (and in partition function form) are 5.2×10^{13} and 4.1×10^{13} s^{-1}, respectively. The other two conformers of the transition state, which are associated with the CF_2Br and CF_2Cl rotors, are 2−3 kcal mol^{-1} above the lowest energy conformer. Except for a few lower frequencies and larger moments of inertia from substitution of the Cl atom by a Br atom, the transition states are very similar for 2,3-FH elimination from $CF_2ClCF_2CH_3$ and $CF_2BrCF_2CH_3$.

The BrF interchange transition state from $CF_2BrCF_2CH_3$ can be compared to the ClF interchange transition state from $CF_2ClCF_2CH_3$.[1−3] Both are bridged structures with halogen atoms roughly equidistant from the two carbon atoms, which have a nearly sp^2 structure. The average of the C−F distances (1.88 Å) is the same for the two transition states. The C−Br distance is longer than C−Cl; however, the fractional extensions (29 and 31%, respectively) of the C−Br and C−Cl bonds are nearly the same. The calculated preexponential factors for the 1,2-BrF and 1,2-ClF unimolecular reactions are 1.2×10^{13} and 1.1×10^{13} s^{-1}, respectively, at 1000 K, and the calculated threshold energies are 58.4 and 62.5 kcal mol^{-1}, respectively, from the 6-311+G(2d,p) basis set.

Since the experimental rate constant for HBr elimination could not be measured, because no $CF_3CFBrCH_3$ was detected, no rate constant calculations were done for either HBr or HF elimination reactions from $CF_3CFBrCH_3$. The branching ratio[10] was 8.7 in favor of HCl over HF elimination from $CF_3CFClCH_3$, and HBr elimination from $CF_3CFBrCH_3$ would be expected to dominate over HF elimination by more than an order of magnitude. The calculated E_0 for HBr loss from $CF_3CFBrCH_3$ was 47.8 kcal mol^{-1} using the 6-311+G(2d,p) basis set compared to an E_0 of 61.6 kcal mol^{-1} for HF elimination and 58.4 kcal mol^{-1} for FBr interchange in $CF_2BrCF_2CH_3$. Thus, collisional quenching of $CF_3CFClCH_3$ would occur in a pressure region approximately 3 orders of magnitude higher[1,11a] than suitable for observing the elimination or interchange reactions of $CF_2BrCF_2CH_3$. Consequently, stabilized $CF_3CFClCH_3$ would never be observed in the present system.

C. Assignment of Threshold Energies. Rice−Ramsperger−Kassel−Marcus (RRKM) rate constants were calculated from the models obtained from DFT calculations. The molecules have two hindered internal rotors and each transition state has one hindered internal rotor, and the torsionsal frequencies were replaced by symmetric hindered rotors for the calculation of the sums and densities of states in eq 6.

$$k_E = \left(s^{\ddagger}/h\right)\left(I^{\ddagger}/I\right)^{1/2}\left(\sum P^{\ddagger}(E - E_0)/N_E^*\right) \qquad (6)$$

The reaction path degeneracies, $s^{\ddagger}$, are 2 for 1,2-BrF interchange and 6 for 2,3-FH elimination. Evaluation of the sums of states, $\sum P^{\ddagger}(E - E_0)$, for the transition state and the density of states, N^*_E, for the molecule were done with the Multi-well code.[23] The overall rotations are considered to be adiabatic, and the ratio of three overall moments of inertia, $(I^{\ddagger}/I)$, is about 1.2. The calculation requires the reduced moment of inertia and the barrier height for each “symmetric” internal rotation. Since the barriers are not experimentally known, they were estimated from the maximum in the torsional potentials, which were 3.0 kcal mol^{-1} for $-CH_3$ and 5.2 and 6.4 kcal mol^{-1} for $-CF_2Br$; see Figure 1 in the Supporting Information. We selected an average barrier of 5.5 kcal mol^{-1} for $-CF_2Br$, which was treated as a symmetric rotor. The I_{red} values were calculated by the method of Pitzer, and the average values are 3.16 (6.25) and 65.3 (70.1) amu Å^2 for the $CH_3(CD_3)$ and CF_2Br groups, respectively. The $I^{\ddagger}_{red}$ values for the transition states were 3.17 (6.32) amu Å^2 for $CH_3(CD_3)$ and 72.5 (75.9) amu Å^2 for CF_2Br. The barrier heights that were used for the molecule also were employed for the transition states. Rate constants were calculated for a range of E_0 with $\langle E \rangle = 96$ kcal mol^{-1}, and the preferred E_0 was selected by matching k_E to the experimental rate constant.

The assigned threshold energies are listed in Table 3; the uncertainties are expected to be ±2.0 kcal mol^{-1}. The threshold energy for 2,3-FH elimination, 66 kcal mol^{-1}, is equal to that from $CF_2ClCF_2CH_3$, 64 kcal mol^{-1}, to within the combined uncertainties. However, the 3-fold smaller experimental rate constant for $CH_2BrCF_2CH_3$, relative to $CH_2ClCF_2CH_3$, does require a higher threshold energy for the former, because substitution of one Br for one Cl does not significantly change the sum of states to density of states ratio in eq 6 for the same E_0. Since the transition state for 1,2-BrF interchange has a smaller entropy than that for 2,3-FH elimination, E_0(1,2-BrF) = 62 kcal mol^{-1} is 4 kcal mol^{-1} lower than E_0(2,3-FH) even though the rate constants are similar. The E_0 values that were assigned to $CF_2BrCF_2CD_3$ are in accord with those for $CF_2BrCF_2CH_3$, since the expected changes in E_0 are 1.0 and 0.07 kcal mol^{-1} for HF (DF) elimination and BrF interchange, respectively, according to zero-point-energy differences. The BrF interchange reaction certainly has a lower threshold energy than the corresponding 1,2-ClF interchange reaction[1] of $CF_2ClCF_2CH_3$, with an $E_0 = 66$ kcal mol^{-1}. It should be noted that lowering the $\langle E(CF_2ClCF_2CH_3) \rangle$ from 98 to 96 kcal mol^{-1} results in a reduction of the E_0 assigned earlier[1] by 1 kcal mol^{-1}.

What are the limitations beyond the assumption behind RRKM theory and selection of the collision cross sections that could affect the E_0 assignments? The $\sum P^{\ddagger}(E - E_0)/N^*_{\mathrm{E}}$ ratio in eq 6 is not sensitive to changes in frequencies provided that the same trend exists for the molecule and the transition state. For example, we tested for the difference between using frequencies of just the lowest energy conformers vs the average of all three conformers (associated with the CF_2Br group) for the HF elimination, and the rate constants differed by less than 20%. Nevertheless, the presence of three conformers means that the assigned value for an E_0 is an average weighted toward the lowest barrier separating reactants and products, and this is one reason that the uncertainty[11a] in E_0 values was quoted as 2 kcal mol^{-1} rather than 1.5 kcal mol^{-1}. One untested assumption is our choice for $V(CH_3)^{\ddagger}$ and $V(CF_2Br)^{\ddagger}$. Provided that the barriers are similar in the transition states and molecule, the actual values do not strongly affect k_E. For example, the calculated rate constants for free-rotor models were very similar (20%) to those of hindered rotor models. The barrier for internal rotation of CH_3 groups is usually close to 3 kcal mol^{-1} and, even if $V(CH_3)^{\ddagger}$ changed by ±1 kcal mol^{-1}, the effect on the rate constant would be minor. If $V(CF_2Br)^{\ddagger}$ was considerably smaller in the 2,3-FH transition state than in the molecule, the calculated rate constant could increase by as much as a factor of 2 (for a free CF_2Br rotor). Such a large difference seems unlikely, but the assumption of $V(CF_2Br) \approx V(CF_2Br)^{\ddagger}$ is untested. As with all chemical activation systems, the uncertainty in the average energy of the activated molecules contributes to the uncertainty in the assigned E_0 values.[11a] For $CF_2ClCF_2CH_3$ and $CF_2BrCF_2CH_3$ this may be the largest contribution to the ±2 kcal mol^{-1} uncertainty.

As previously noted, the structure of the transition state shown in Figure 3 for BrF interchange is similar to the bridged structure for ClF interchange in $CF_2ClCF_2CH_3$. In both cases the rearranged product, $CF_3CFBrCH_3$* or $CF_3CFClCH_3$*, acquires ≈3 kcal mol^{-1} additional energy and 2,3-BrH or 2,3-ClH elimination gives the observed $CF_3CF{=}CH_2$ product without collisional stabilization of $CF_3CFBrCH_3$* or $CF_3CFClCH_3$*. Although the B3PW91/6-311+G(2d,p) method has not been tested for molecules (or transition states) containing Br atoms, it is worth comparing the calculated threshold energies to the experimentally based assignments. As might be expected based on previous comparisons for HF elimination,[1,4,9−11] the calculated E_0(2,3-FH) of 62 kcal mol^{-1} is below the experimentally assigned value of 66 kcal mol^{-1}. The calculated value for E_0(1,2-BrF) is 58.4 kcal mol^{-1}, and it has a similar discrepancy with the experimentally assigned value. This discrepancy also existed for the calculated E_0(1,2-ClF) values for $CF_2ClCF_2CH_3$ and $CF_2ClCHFCH_3$.[7] Although further work[13] is needed to find the best theoretical method and the best basis set for treating unimolecular reactions of molecules in which Br atoms are involved in the reaction coordinate, the results from the B3PW91/6-311+G(2d,p) method provided a respectable framework for interpretation of the $CF_2BrCF_2CH_3$ data.

V. Conclusions

The 1,2-BrF interchange reaction has been demonstrated for $CF_2BrCF_2CH_3$ (CD_3) molecules formed with 96 kcal mol^{-1} vibrational energy from the recombination of CF_2BrCF_2 and CH_3 (CD_3) radicals. The BrF interchange reaction is in competition with 2,3-FH (FD) elimination. There was no evidence for a significant C−Br rupture pathway.[24] Matching calculated RRKM rate constants to experimental rate constants gave threshold energies of 62 and 66 kcal mol^{-1} for BrF interchange and HF elimination, respectively. The kinetic isotope effects for both reaction channels support these threshold energy assignments. Comparison with reactions of $CF_2ClCF_2CH_3$[4] shows that the threshold energy for 1,2-BrF interchange is ≈4 kcal mol^{-1} lower than for 1,2-ClF interchange. Given the low threshold energy, the interchange of Br and F atoms, or Br and Cl atoms,[25] that are located on adjacent carbon atoms can be expected to be important for vibrationally excited bromofluoro- and chlorobromoalkane molecules, provided that competing HBr elimination or C−Br rupture pathways are not dominant. The threshold energies for 2,3-FH elimination (64−66 kcal mol^{-1}) are similar for $CF_2BrCF_2CH_3$ and $CF_2ClCF_2CH_3$, as well as for $CF_3CF_2CH_3$.[9] It should be remembered that the assigned E_0 values for FH elimination from $CF_2ClCF_2CH_3$ and $CF_2BrCF_2CH_3$ are average values for three conformers of the transition state.

DFT calculations at the B3PW91/6-311+G(2d,p) level for the lowest energy conformers gave a threshold energy for 2,3-FH elimination of 61.6 kcal mol^{-1}, which is somewhat below the experimental assignment, as has been found for several other 2,3-FH elimination reactions.[26] The calculated threshold energy for BrF interchange also is too low, as was the case for ClF interchange in $CF_2ClCF_2CH_3$ and $CF_2ClCHFCH_3$. However, the calculations do give the correct difference between E_0(ClF) and E_0(BrF). Further exploration of methods and basis sets is needed to find the best computational method for the threshold energies of halogen atom interchange reactions; however, the current DFT calculation seemed to define a realistic structure of the transition state for Br−F interchange.[27]

The photolysis of CF_2BrCF_2I at ≥280 nm from a high-pressure Hg lamp provided a satisfactory source of gas-phase CF_2BrCF_2 radicals at room temperature.

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Supporting Information Available: Table 1 lists the frequencies, overall moments of inertia, and the reduced moments of inertia and shows the geometries for (a) all rotomers for $CF_2BrCF_2CH_3$, (b) all rotomers for $CF_2BrCF_2CD_3$, (c) the rotomers for the 2,3-FH transition states, (d) the rotomers for the 2,3-DF transition states and (e) the FBr interchange transition states. Figure 1 shows the barrier heights for internal rotation and reduced moments of inertia for $CF_2BrCF_2CH_3$ and $CF_2BrCF_2CD_3$ calculated using DFT method with B3PW91/6-311g-(2d,p) level of theory and basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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