Unimolecular Reactions of CH₂BrCH₂Br, CH₂BrCH₂Cl, and CH₂BrCD₂Cl: Identification of the Cl–Br Interchange Reaction

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The recombination reactions of CH₂Br and CH₂Cl radicals have been used to generate vibrationally excited CH₂BrCH₂Br and CH₂BrCH₂Cl molecules with 91 kcal mol⁻¹ of energy in a room-temperature bath gas. The experimental unimolecular rate constants for elimination of HBr and HCl were compared to calculated statistical rate constants to assign threshold energies of 58 kcal mol⁻¹ for HBr elimination from C₂H₄Br₂ and 58 and 60 kcal mol⁻¹, respectively, for HBr and HCl elimination from C₂H₄BrCl. The Br–Cl interchange reaction was demonstrated and characterized by studying the CH₂BrCD₂Cl system generated by the recombination of CH₂Br and CD₂Cl radicals. The interchange reaction was identified from the elimination of HBr and DCl from CH₂BrCD₂Cl, and a threshold energy of \approx 43 kcal mol⁻¹ was assigned to the interchange reaction. The statistical rate constants were calculated from models of the transition states that were obtained from density functional theory using the B3PW91 method with the 6-31G(d',p') basis set. The model for HBr elimination was tested versus published thermal and chemical activation data for C₂H₅Br. A comparison of Br–Cl interchange reaction in 1,2-haloalkanes is presented.

I. Introduction

The Cl-F interchange reaction for chlorofluoroalkane molecules with adjacent fluorine and chlorine atoms has been characterized for several fluorochloroethanes,^{1,2} -propanes,³⁻⁷ and -butanes.⁸ The threshold energies are in the 60-70 kcal mol⁻¹ range. The Br-F interchange reaction also has been characterized for CF2BrCF2CH3 for comparison to Cl-F interchange in similar compounds.9 We now have turned our attention to the Cl-Br interchange reaction in 1,2-chlorobromoethane. The chemical activation technique was used to generate CH₂BrCH₂Br, CH₂BrCH₂Cl, and CH₂BrCD₂Cl molecules with 91 kcal mol⁻¹ of vibrational energy by the recombination reactions of CH2Br and CH2Cl (CD2Cl) radicals at room temperature. These radicals were obtained from the photolysis of CH₂BrI and CH₂ClI (CD₂ClI). The Cl-Br interchange was detected from the conversion of CH2BrCD2Cl into CH₂ClCD₂Br. Just as the Cl-F interchange reaction was in competition with HCl and HF elimination reactions for the fluorochloroalkanes, Cl-Br interchange is in competition with HBr (DBr) and HCl (DCl) elimination reactions. Therefore, the CH2BrCH2Br and CH2BrCH2Cl systems were used to characterize the HBr and HCl elimination processes as a necessary part of the study of Cl-Br interchange. The HCl elimination reaction from CH2BrCH2Cl also can be compared to that of CH₂ClCH₂Cl¹⁰ to gain more information about the unimolecular reactions of 1,2-dihaloethanes.¹⁰ The chemically activated CH2BrCH2Br and CH2BrCH2Cl molecules have been studied previously,¹¹ but the chemical system was complicated, and the new data are an improvement.

The experimental rate constants for molecules with 91 kcal mol⁻¹ of vibrational energy were compared to calculated statistical (RRKM) unimolecular rate constants to assign threshold energies (E_0) to HCl and HBr elimination and to Cl-Br interchange. The channel with the lowest threshold energy for CH₂BrCH₂Cl is actually the Cl-Br interchange. The RRKM rate constants are based upon density functional theory (DFT) calculations for the vibrational frequencies and moments of inertia of the molecule and transition state. We have continued to use the B3PW91 method with either the 6-31G(d',p') or 6-311+G(2d,p) basis sets.^{3-10,12} The complex torsional mode of these molecules was treated as an asymmetric, hindered, internal rotation for the calculation of the rate constants.¹⁰ The rate constants for DCl and DBr elimination from CH2BrCD2Cl and CH₂ClCD₂Br were calculated from the models developed for CH₂BrCH₂Cl.

Because DFT calculations for transition states involving HBr elimination or other processes involving Br-atoms have not been extensively explored, 9,13,14 we decided to test the method that our laboratory has employed for Cl-F interchange and HCl and HF elimination reactions by comparing calculated rate constants to published experimental data for the C₂H₅Br reaction. Although some uncertainty may exist for the experimental thermal¹⁵⁻¹⁸ and chemical activation¹¹ rate constants, the C₂H₅Br reaction can serve as a baseline test for the transition-state structure for HBr elimination. Comparison also can be made for trends in the C₂H₅F, C₂H₅Cl, and C₂H₅Br series. For example, the threshold energies are known to decline by about 3 kcal mol^{-1} for each member in the series, that is, 58, 55, and 52 kcal mol⁻¹. Modest agreement between experimentally determined Arrhenius pre-exponential factors and those from electronic-structure calculations exist for HF elimination when the torsional mode(s) are treated as hindered internal rotations.^{10,12} However, the calculated transition-state models for HCl elimina-

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tion may overestimate the Arrhenius pre-exponential factors by a factor of 2,^{10,12} which is near the limit of the experimental uncertainty given the limited temperature ranges of the individual investigations. Thus, it is of interest to extend the comparison to the HBr elimination reaction of C₂H₃Br.

The experiments with $C_2H_4Br_2$ utilized the photolysis¹⁹ of CH_2BrI to generate CH_2Br radicals in a clean environment; C_4F_{10} was added to achieve higher pressures. The recombination reaction gives $CH_2BrCH_2Br^*$; the asterisk denotes vibrational excitation.

$$CH_2Br + CH_2Br \rightarrow CH_2BrCH_2Br^*$$
 (1a)

$$CH_2BrCH_2Br^* \rightarrow HBr + CH_2 = CHBr (D)$$
 (1b)

$$+ C_4 F_{10} \rightarrow CH_2 Br CH_2 Br (S)$$
(1c)

The threshold energy for Br atom dissociation is 70 kcal mol^{-1} , and dissociation is not competitive with HBr elimination from CH₂BrCH₂Br molecules with 91 kcal mol^{-1} of energy. Reaction 1b is 20 kcal mol^{-1} endothermic, and CH₂=CHBr will be stabilized by collisions for the pressures of our experiments.

The experiments for CH_2BrCH_2Cl (and CH_2BrCD_2Cl) utilized the photolysis of CH_2BrI and CH_2ClI (CD_2ClI) in SF_6 bath gas. The radical recombination reactions are 1, 2, and 3.

$$CH_2Br + CH_2Cl \rightarrow CH_2BrCH_2Cl^*$$
 (2a)

$$CH_2BrCH_2Cl^* \rightarrow HBr + CH_2=CHCl(D_1)$$
 (2b)

$$\rightarrow \text{HCl} + \text{CH}_2 = \text{CHBr}(D_2) \qquad (2c)$$

$$+ SF_6 \rightarrow CH_2BrCH_2Cl(S) + SF_6 \qquad (2d)$$

$$CH_2Cl + CH_2Cl \rightarrow CH_2ClCH_2Cl^*$$
 (3a)

$$CH_2ClCH_2Cl^* \rightarrow HCl + CH_2 = CHCl (D)$$
 (3b)

$$+ SF_6 \rightarrow CH_2ClCH_2Cl(S) + SF_6$$
 (3c)

The unimolecular rate constants were measured relative to collisional deactivation. The slopes from plots of the ratio of decomposition to stabilization products (D/S) versus pressure⁻¹ for a range of pressure such that D/S ≤ 1.0 give rate constants, after conversion to units of s⁻¹, that are equivalent to $k_{<E>}$. The assumption implied by eqs 1c, 2d, and 3c for efficient collisional deactivation will be addressed in the section discussing studies of the C₂H₅Br reaction. The rate constant for C₂H₄Cl₂* previously has been measured^{20,21} in SF₆ bath gas as 21 ± 3 torr, which corresponds to 3.1 × 10⁸ s⁻¹.

The Cl–Br interchange reaction was identified from deuterium labeling of CH₂BrCD₂Cl and the possible reactions are enumerated in 4.

$$CH_2BrCD_2Cl^* \rightarrow DBr + CH_2 = CDCl(D_1)$$
 (4a)

$$\rightarrow$$
 HCl + CHBr=CD₂ (D₂) (4b)

$$\rightarrow CH_2ClCD_2Br^*$$
 (4c)

$$+ SF_6 \rightarrow CH_2BrCD_2Cl(S)$$
 (4d)

$$CH_2ClCD_2Br^* \rightarrow HBr + CHCl=CD_2(D_1)$$
 (4e)

$$\rightarrow$$
 DCl + CH₂=CDBr (D₂) (4f)

$$\rightarrow CH_2BrCD_2Cl^*$$
 (4g)

$$+ SF_6 \rightarrow CH_2 ClCD_2 Br(S)$$
 (4h)

The recombination reactions also give $C_2D_4Cl_2^*$ and $C_2H_4Br_2^*$, and their decomposition products must be considered in the analysis of vinyl chloride and vinyl bromide. The decomposition of $CH_2BrCD_2Cl^*$ gives $DBr (+ CH_2=CDCl)$ and $HCl (+ CD_2=CHBr)$, whereas $CH_2ClCD_2Br^*$ gives HBr (+ $CD_2=CHCl$) and DCl (+ $CH_2=CDBr$) and each channel can be identified from the vinyl chloride- d_1 or $-d_2$ and vinyl bromide d_1 or $-d_2$ by gas chromatography with mass spectrometric detection. In anticipation of the results to be presented, the Cl-Br interchange reaction is ≈ 8 times faster than the sum of the elimination reactions of CH_2BrCD_2Cl .

II. Experimental Methods

The CH₂BrI and CH₂ClI were purchased from Acros and CD₂CII was purchased from CDN Isotopes with a stated isotopic purity of 99.9% D. The C_4F_{10} and SF_6 were both obtained from PCR (now SynQuest). The reagents and bath gases were measured in calibrated volumes on a grease-free vacuum line and transferred cryogenically to Pyrex vessels ranging in size from 3.88 to 24.88 cm³ for photolysis. The ratios of bath gas to reagent were \geq 50. Some experiments were done in larger vessels to achieve low pressure for the experiments with CH₂BrCD₂Cl. A small amount of mercury(I) iodide was added to each vessel to aid in the generation of radicals²² and to remove HCl and HBr. Pressures were measured with a MKS electronic manometer. Each vessel was irradiated for about 5 min with the output of a 200 W high-pressure mercury lamp. The Pyrex vessel acted as a filter to limit the effective photolysis wavelength to 290-330 nm. In this wavelength range the upper electronic state dissociates only by rupture of the CH₂Br-I and CH₂Cl-I bonds.¹⁹

After photolysis, the samples for the CH₂BrCH₂Br or the CH₂BrCH₂Cl systems were analyzed for products with a Shimadzu 14A gas chromatograph fitted with a 105 m RTX-VGC column of 0.53 mm diameter. For measurement of decomposition to stabilization ratios (D/S), a flame-ionization detector (GC-FID) was used. The temperature program with the GC-FID for analysis of both the C2H4Br2 and CH2BrCH2Cl systems was 20 min at 30 °C followed by a temperature increase of 6 °C/min until the final temperature of 180 °C was attained. The characteristic retention times (in minutes) were 11.1 for CH₂=CHCl, 14.9 for CH₂=CHBr, 39.5 for C₂H₄ClBr, and 44 for C₂H₄Br₂. The problem of interference in the measurements of vinyl chloride or vinyl bromide from reactions 1b or 3b in the study of C₂H₄ClBr was avoided by using large starting ratios of CH₂BrI/CH₂CII when observing vinyl chloride and large ratios of CH₂ClI/CH₂BrI when observing vinyl bromide. A similar approach has been described¹⁰ for the CH₂FCH₂Cl system, and more details are provided in Section III-A. Calibration factors for the GC-FID were experimentally determined from prepared mixtures of CH₂=CHCl, CH₂=CHBr, C_2H_4ClBr , $C_2H_4Cl_2$, and $C_2H_4Br_2$. The factors were 1.10 ± 0.12 $(CH_2=CHBr/C_2H_4Br_2)$, 1.09 \pm 0.11 (C_2H_3Cl/C_2H_4ClBr) , and 1.11 ± 0.12 (C₂H₃Br/C₂H₄ClBr), which were applied to the experimentally measured ratios to obtain the actual ratios of concentrations. The SF₆ is not sensed by the GC-FID, the



Figure 1. Plot of $C_2H_3Br/C_2H_4Br_2$ vs pressure⁻¹ for the $C_2H_4Br_2$ system. The slope and intercept of the line are 112 ± 8 torr and -0.05 ± 0.04 , respectively. The correlation coefficient is 0.94.

detector is not very sensitive to C_4F_{10} , and CH_2BrI and CH_2CII were not monitored.

For analysis of vinyl chloride and vinyl bromide in the CH₂BrCD₂Cl system, the FID detector was replaced by a massspectrometer detector (GC-MS) containing a 0.25 mm by 105 m RTX-VMS column. The temperature program for the GC-MS analysis of vinyl chloride- d_1 , $-d_2$, and vinyl bromide- d_1 , $-d_2$ began with 15 min at 35 °C followed by a temperature increase of 12 °C/min to a final temperature of 180 °C. The retention times were 7.0 and 9.4 min for vinyl chloride and vinyl bromide, respectively. Additional details about the mass spectrometric analysis are given in Section III-B.

III. Experimental Results

A. Rate Constants for CH₂BrCH₂Br and CH₂BrCH₂Cl. The analysis for the C₂H₃Br and C₂H₄Br₂ products from the photolysis of CH₂BrI was straightforward, and 29 measurements were made over the pressure range of 100-1000 torr with C₄F₁₀ as the bath gas. The resulting C2H3Br/C2H4Br2 (or D/S) ratios are plotted versus pressure⁻¹ in Figure 1. As is evident from inspection of the plot, experiments in triplicate or quadruplicate usually were done at a given pressure. The least-squares linear fit to the plot gives a slope of 112 ± 8 torr. The linear plot has a small negative intercept. If the line is forced to pass through the origin, the slope would decline to 104 \pm 8 torr. This experimental result can be compared to the measurement made in 1967 in a more complex chemical system (the reaction of CH_2 with CH_2Br_2) with CF_4 as the bath gas. The slope of the D/S plot reported for $C_2H_4Br_2^*$ was 220 \pm 30 torr. After allowance for the difference in collisional efficiencies of CF₄ versus C_4F_{10} , a factor of 1.4–1.5 for the high-pressure rate constant, the 1967 result would correspond to 150 ± 20 torr for a collider similar to C₄F₁₀. The two measurements are nearly within their combined experimental uncertainties. However, the current measurement is certainly preferred. The rate constant for C₂H₄Br₂* is approximately 6 times larger than that for $C_2H_4Cl_2^*$.

The photolysis of CH₂BrI/CH₂ClI mixtures gives $C_2H_4Br_2^*$ and $C_2H_4Cl_2^*$, as well as $C_2H_4ClBr^*$. The rate constants for formation of vinyl chloride from $C_2H_4Cl_2^*$ and vinyl bromide from $C_2H_4Br_2^*$ are large enough that excluding vinyl bromide from reaction 1b and vinyl chloride from 3b is necessary. To



Figure 2. Plots of D/S vs pressure⁻¹ for the C₂H₄ClBr system. \blacksquare : CH₂=CHCl/C₂H₄ClBr; the slope and intercept of the line are 75.7 \pm 5.8 torr and -0.03 ± 0.04 , respectively, the correlation coefficient is 0.95. \bullet : CH₂=CHBr/C₂H₄BrCl; the slope and intercept of the line are 32.6 \pm 0.7 torr and -0.06 ± 0.01 , respectively, the correlation coefficient is 0.99.

obtain the rate constants for just reactions 2a and 2b, two series of experiments were done with 8:1 ratios of CH2BrI vs CH2ICl to measure vinyl chloride from C2H4BrCl* and 20:1 ratios of CH₂ClI vs CH₂BrI to measure vinyl bromide from C₂H₄BrCl*. Nineteen experiments to measure the rate constant for loss of HBr were done over the 70–600 torr pressure range with SF_6 as the bath gas, and the results are shown in Figure 2. The leastsquares fit to the points give a slope of 75.7 ± 5.8 torr. Twentysix experiments were done over the pressure range of 25-280 torr of SF_6 to measure the rate constant for reaction 2c and the results are shown in Figure 2. The slope of the line, which corresponds to the elimination of HCl from CH₂BrCH₂Cl, is 32.6 ± 0.7 . The sum of the two rate constants is 108 torr, and the total rate constants for $C_2H_4Br_2^*$ and $C_2H_4BrCl^*$ are equal. The ratio of rate constants for C₂H₄BrCl* is 2.3 in favor of HBr elimination. Changing the ratios of the iodide precursors as explained above was very successful in isolating the reaction of interest. The rate constants for C₂H₄Br₂ and C₂H₄BrCl are summarized in Table 1. The collision diameters and Lennard-Jones well-depth parameters that were used to calculate the collision rate constant, for converting the slopes of the D/S plots to s^{-1} , are given in the footnotes of the table. The measured rate constants also are adjusted to unit deactivation in Table 1. Estimates of the two rate constants for CH₂ClCH₂Br* were also provided in the 1967 work. They were measured by an indirect method, and the values seem to be too small by a factor of 2, even though the ratio of rate constants is the same as that deduced from the data in Figure 2. The rate constant for HCl elimination from CH₂BrCH₂Cl* is 1.5 times larger than that from C₂H₄Cl₂*, which implies that the threshold energy for HCl elimination is lower for C₂H₄BrCl.

B. Evidence for Cl–Br Interchange in CH₂BrCD₂Cl. The rate constants for CH₂BrCD₂Cl* and CH₂ClCD₂Br* will be reduced^{23–25} by approximately a factor of 2 for DCl or DBr elimination (a combined primary and secondary kinetic-isotope effect) and 1.5 for HCl or HBr elimination (a secondary kinetic-isotope effect) relative to CH₂BrCH₂Cl*. Thus, the overall pressure range for a similar degree of decomposition of

TABLE 1: Rate Constants and Threshold Energies for C₂H₄Br₂ and C₂H₄BrCl

		rate constants, (s ⁻¹)		
molecule	slopes of D/S plots (torr) ^a	experimental ^{a,d}	calculated	E_0 (kcal mol ⁻¹)
CH ₂ BrCH ₂ Br(-HBr)	$112\pm8^{b,d}$	$1.7 \pm 0.3 imes 10^9 \ (1.5 imes 10^9)^e$	2.0×10^9 1.5×10^9	58 59
CH ₂ BrCH ₂ Cl(-HBr)	$75.7 \pm 5.8^{c,d}$	$1.0 \pm 0.2 \times 10^9 \ (0.74 \times 10^9)^e$	1.1×10^9 0.84×10^9	58 59
(-HCl)	$32.6 \pm 0.7^{c,d}$	$0.45 \pm 0.07 \times 10^9 \ (0.32 \times 10^9)^e$	0.55×10^9 0.40×10^9	60 61
CH ₂ BrCD ₂ Cl (-DBr) (-HCl) CH ₂ ClCD ₂ Br (-HBr)			$(0.49 \times 10^9)^f (0.34 \times 10^9)^f (0.74 \times 10^9)^f (0.22 \log 10^9)^f (0.21 \log 10^9)^f (0.21 \log 10^9)^f (0.21 \log 10^9)^f (0.22 \log 10$	59.1 60.2 58.2
(-DCI)			(0.23×10^{5})	01.1

^{*a*} The slopes were converted to rate constants by changing the pressure to concentrations (molecules/cm³) and multiplying by the collision rate constant, $k_{\rm M}$. ^{*b*} In C₄F₁₀ bath gas; the σ and ε/k are 6.3 Å and 247 K; see ref 26. ^{*c*} In SF₆ bath gas; the σ and ε/k are 5.2 Å and 212 K; see ref 26. ^{*d*} The σ and ε/k for C₂H₄Br₂ are 5.5 Å and 465 K, and for C₂H₄BrCl they are 5.2 Å and 484 K; see ref 26. ^{*e*} The measured rate constants were reduced by factors of 0.88 and 0.71 for C₄F₁₀ and SF₆, respectively, to obtain unit deactivation rate constants given in parentheses. ^{*f*} Calculated rate constants deduced from the model developed for CH₂ClCH₂Br using E_0 (HCl) = 60 kcal mol⁻¹ and E_0 (HBr) = 58 kcal mol⁻¹; see text for explanation. The calculations are for the hindered-rotor model with the three overall rotations taken as adiabatic.

CH2BrCD2Cl* will be shifted to lower pressures by a factor of \approx 2 relative to the data in Figure 2. All experiments were done with SF₆ bath gas, and large vessels were used to achieve low pressures. Two series of experiments were done. For the first series, the pressure was sufficiently low that decomposition of C2H2D2ClBr* molecules would have been nearly complete, for example, S/D \leq 0.05. If the rate of Br/Cl interchange is competitive with the rates of elimination, products from reactions 4e and 4f will be present. The degree of interchange can be measured by the ratios of HCl/DCl (CHBr=CD₂/ CDBr=CH₂) and HBr/DBr (CHCl=CD₂)/CDCl=CH₂). Before describing the results of the experiments, the GC-MS analysis of the isotopes of vinyl bromide and vinyl chloride needs to be discussed. It should be noted that C2D4Cl2* and C2H4Br2* also are products in these experiments and the composition of the products from decomposition of C₂D₄Cl₂*, C₂H₄Br₂*, and C₂H₂D₂BrCl* will change with pressure.

The vinyl chloride sample delivered to the mass spectrometer will be a mixture of C₂D₃Cl, CHCl=CD₂ and CDCl=CH₂. Due to the ³⁵Cl (75.8%) and ³⁷Cl (24.2%) isotopes, this mixture has masses of 65 and 67 (for C_2D_3Cl), 64 and 66 (for CD_2 =CHCl), and 63 and 65 (for CDCl=CH₂). The contribution to mass 65 from C₂D₃Cl was removed from the mass spectrum of the mixture by measuring the ratio of 65 and 67 from C₂D₃Cl alone, which was generated from the decomposition of $C_2D_4Cl_2$ from the photolysis of CD₂CII. With this ratio and with the signal from mass 67 from the mixture, the contribution to mass 65 from C₂D₃Cl could be subtracted to obtain just the signal for just CDCl=CH2. The ratio of CD2=CHCl/CDCl=CH2 could be assigned as the ratio of the sum of the mass peaks (64 + 66): (63 + 65) or as just the ratio of mass peaks 64:63. The situation for vinyl bromide is similar, since ⁷⁹Br (50.7%) and ⁸¹Br (49.3%) isotopes exist. The masses present in a photolyzed sample are 110 and 108 (for CD₂=CHBr), 109 and 107 (for CDBr=CH₂), and 106 and 108 (for C₂H₃Br). The contribution to mass peak 108 from C₂H₃Br could be subtracted after measurement of the106/108 ratio from a pure sample of C₂H₃Br. Therefore, the ratio of CD₂=CHBr/CDBr=CH₂ could be assigned as the ratio of the sum of masses (109 + 107)/(110 + 108) or as the ratio of 110:109.

The data are presented in Figure 3 for experiments over two pressure regimes; 0.25-3.5 torr and 13-62 torr. Below 3.5 torr the decomposition of CH₂BrCD₂Cl*(CH₂ClCD₂Br*) will be higher than 90%. The interchange reaction certainly has occurred because appreciable quantities of CH₂=CDBr and CHCl=CD₂



Figure 3. Plots of the $k_{\text{HCI}}/k_{\text{DCI}}$ (\bullet : CHBr=CD₂/CH₂=CDBr) and $k_{\text{HBr}}/k_{\text{DBr}}$ (\blacksquare : CHCl=CD₂/CH₂=CDCl) product ratios from CH₂BrCD₂Cl and CH₂ClCD₂Br vs pressure.

are observed with ratios of CHCl=CD₂/CH₂=CDCl = $1.14 \pm$ 0.03 and CHBr=CD₂/CH₂=CDBr = 1.65 ± 0.07 for the experiments below 5 torr. The next series of experiments included photolysis at 13, 20, 32, and 62 torr to explore the effects of partial collisional stabilization of CH₂BrCD₂Cl* and CH₂ClCD₂Br* on the ratios of products. The D/S ratio should be about 1 at 60 torr. Within the experimental uncertainty, the vinyl chloride ratio is 1.14 ± 0.04 and did not change over this pressure range. The vinyl bromide ratio for the four trials at 62 torr is 1.74 ± 0.04 , which is slightly higher than the average at low pressure. However, the vinyl bromide ratio is 1.67 ± 0.06 for the 13-62 torr pressure range, the same as the average at low pressure. If collisoional deactivation influences the product branching in the system, it must affect both ratios. Since loss of DCl has the slowest rate, CH₂=CDBr has the smallest yield and is subject to the highest uncertainty. We conclude that up to 60 torr, the ratio of HCl/DCl and HBr/DBr is nearly constant, that is, the interchange rate constant is considerably larger than the elimination rate constants. After the elimination constants are assigned from calculations of the kinetic-isotope effects for

CH₂BrCD₂Cl and CH₂ClCD₂Br, an estimate is provided for the interchange rate constant in Section IV-C.

C. Thermochemistry. The average vibrational energy of the $C_2H_4Br_2$ molecules formed by reaction 1a can be evaluated from eq 5, assuming that the activation energy for CH₂Br recombination is nearly zero.

$$\langle E(C_2H_4Br_2) \rangle = D_0(CH_2Br-CH_2Br) + 3RT + 2\langle E_V(CH_2Br) \rangle$$
 (5)

The last term is the thermal vibrational of the CH2Br radicals at room temperature. The D₂₉₈(CH₂-CH₂Br) value can be obtained from the enthalpies of formation of C2H4Br2 and CH2Br at 298 K, which are -9.0^{27} and 40.9^{28} kcal mol⁻¹, respectively. These numbers give $D_{298}(CH_2Br-CH_2Br) = 90.8 \text{ kcal mol}^{-1}$. which becomes 89.3 kcal mol⁻¹ at 0 K, and $\langle E(C_2H_4Br_2) \rangle$ is 91.8 kcal mol⁻¹. The same procedure for CH₂BrCH₂Cl gives an average energy of 90.7 kcal mol⁻¹, based on enthalpies of formation at 298 K of 28.0 and -21.0 for CH₂Cl^{29a} and C₂H₄ClBr,^{29b} respectively. A recent computational study³⁰ reported the enthalpy of formation of CH₂Br at 298 K as 39.8 kcal mol⁻¹. This value would lower the average energies of $C_2H_4Br_2$ and C_2H_4BrCl by 2 and 1 kcal mol⁻¹, respectively, and make them equal. Therefore, we will take both average energies to be 91 kcal mol⁻¹. Given the reliability of the thermochemistry, the uncertainty in $\langle E \rangle$ should be ± 2 kcal mol^{-1} .

IV. Computational Results

A. Models for Molecules, Transition States, and Calculated Rate Constants. Electronic structure calculations were done for the molecules and transition states using DFT with the B3PW91 method and 6-31G(d',p') basis set. In some cases supporting calculations were done with the 6-311+G(2d,p) basis set. The calculated moments of inertia and frequencies closely matched the experimental results for $C_2H_5Br^{31}$ and other calculated results for C₂H₄Br₂.³² The torsional motion of the CH2BrCH2Br and CH2BrCH2Cl molecules is the only unusual aspect of the structures. For calculation of the density of states, the torsion was treated as an asymmetric, hindered, internal rotation. The molecules have trans and gauche conformers; the trans-conformer is 1.8 kcal mol⁻¹ lower in energy. Wong et al.³³ evaluated the potential for the hindered internal-rotation of C₂H₄Br₂ and calculated the energy levels below the barriers, which are 5.5 and 9.7 kcal mol⁻¹, as well as those above the barriers. They kindly provided us with a listing of the energy levels, and we combined them with the vibrational sums of states to obtain the total sums and density of states for C₂H₄Br₂. These densities also were compared to the result from treating the torsion as a hindered symmetric rotor with a barrier equal to the average of the two actual barriers. The energy levels for the hindered internal rotor of CH₂BrCH₂Cl were not evaluated by Wong et al. Therefore, we calculated the potential function using the 6-31G(d',p') basis set. The potential energy barriers were 4.6 and 8.6 kcal mol⁻¹, and the energy difference between the conformers was 1.7 kcal mol⁻¹. We averaged the two barriers and calculated the density of states for CH₂BrCH₂Cl as for an equivalent symmetric internal rotor with a barrier of 6.6 kcal mol⁻¹. The reliability of the barriers from the calculation for C₂H₄BrCl was confirmed by doing a calculation of the potential for C2H4Br2 and comparing the result to other calculations.^{32,33} Upon the basis of four examples, including that for C₂H₄Br₂, the symmetric-rotor approximation for C₂H₄BrCl should be within 15-20% of the density of states using the explicit energy levels of the asymmetric-rotor.¹⁰ In addition to the C₂H₄Br₂ and C₂H₄BrCl systems, calculations also were done for C₂H₅Br as a reference for HBr elimination. In this case the hindered internal rotation is a symmetric CH₃ rotor and evaluation of the density of states is straightforward. The calculated frequencies, moments of inertia, and structures for the transition states are shown in the Supporting Information. All electronic structure calculations were done with the Gaussian 03 suite of codes.³⁴

The calculated threshold energies, in kcal mol⁻¹, from the 6-31G(d',p') basis set were 53.7, C₂H₅Br; 57.5, CH₂BrCH₂Br; and 58.1, 57.7, 41.8 and CH₂BrCH₂Cl for the HCl, HBr, and interchange channels, respectively. The predicted increase in E_0 for HBr elimination from the dihalides relative to C₂H₅Br should be noted, as well as the very low E_0 for the interchange reaction.

The density of states, $N^*(E)$, for the molecules and the sums of states for the transition state, $\Sigma P^{\dagger}(E - E_0)$, were used in the RRKM equation below to calculate the rate constants.

$$k_E = s^{\dagger} / h (I^{\dagger} / I)^{1/2} \Sigma P^{\dagger} (E - E_0) / N^* (E)$$
(6)

The reaction path degeneracy is s^{\dagger} , and I^{\dagger}/I is the ratio of overall moments of inertia. For $C_2H_4Br_2$, $s^{\dagger} = 4$; and for $C_2H_4BrCl s^{\dagger} = 2$ for HCl and for HBr elimination. The moments of inertia and the reduced moment for internal-rotation, Ired, change with conformer and with internal rotation in general. Therefore, we used the average values of I, I_{red} , and vibrational frequencies from calculations of the molecular structure of $C_2H_4Br_2$ for each 20° of rotation. The average I_{red} and $(I^{\uparrow}/I)^{1/2}$ values were 28.7 amu Å² and 1.38 for C₂H₄Br₂. For C₂H₄BrCl, the frequencies and moments of inertia were calculated for the two conformers and the two barriers; the resulting average values were $I_{\text{red}} = 19.2$ amu Å and $(I^{\dagger}/I)^{1/2} = 1.32$ (HCl elimination), 1.36 (HBr elimination), and 0.91 (Br/Cl interchange). The transition-state structures for HBr elimination, HCl elimination, and Br/Cl interchange were obtained from the Gaussian code in the usual way.⁵⁻¹⁰ The rate constants were calculated using the Multiwell $code^{35}$ after the $N(E^*)$ were obtained. As points of reference, rate constants also were calculated from $N(E^*)$ with the torsional mode treated as a vibration and as a freerotor.

After the $E_0(\text{HCl})$ and $E_0(\text{HBr})$ values were assigned for C₂H₄BrCl from matching $k_{\langle E \rangle}$ and $k_{\exp p}$, the calculated zero-point energies were used to assign threshold energies to the reactions of CH₂BrCD₂Cl and CH₂ClCD₂Br. In fact, $E_0(\text{HCl})$ and $E_0(\text{HBr})$ were nearly the same as for C₂H₄BrCl, and $E_0(\text{DCl})$ and $E_0(\text{DBr})$ were higher by 1.1 kcal mol⁻¹. The threshold energy for Br/Cl interchange, which was assigned from fitting the data in Section III-B, was the same for CD₂ClCH₂Br and CH₂ClCD₂Br. The frequencies and moments of inertia needed to obtain the sums and densities of states in eq 6 for CH₂BrCD₂Cl and CD₂BrCH₂Cl were obtained from the Gaussian code following the same procedure as described for CH₂BrCH₂Cl.

B. Comparison of Calculated and Experimental Results for C₂H₅Br. The model for the HBr elimination reaction from C₂H₅Br can be tested using the published results from thermal and chemical-activation studies. The two most recent thermal studies reported limiting high-pressure Arrhenius parameters of $10^{13.62\pm0.22} \exp(-53.4 \pm 0.7 \text{ kcal mol}^{-1}/RT)^{15}$ from a temperature range of 660–706 K and $10^{13.6\pm0.3} \exp(-52.8 \pm 1.0 \text{ kcal mol}^{-1}/RT)^{16}$ from a temperature range of 950–1200 K. These results are in agreement with a shock-tube study¹⁷ over the temperature range of 740–1000 K, which reported $10^{13.3} \exp(-53.5 \text{ kcal})$ mol^{-1}/RT) and also with early pyrolysis studies.¹⁸ All of these Arrhenius parameters could be criticized, for example the work of ref 15 covers a very small temperature range, and that of ref 16 is an extrapolation from very-low-pressure pyrolysis experiments. Also, some early measurements may not have been in the true high pressure limit.¹¹ Tsang¹⁷ selected isopropyl bromide as the reference reaction for his shock-tube work, and two subsequent studies have confirmed his selection of Arrhenius parameters for isopropyl bromide.^{36,37} Hippler et al.³⁸ combined their data with published results for *t*-butyl bromide to provide an Arrhenius plot encompassing 9 orders of magnitude in the rate constant. Their global fit gave Arrhenius parameters for *t*-butyl bromide that were slightly higher than those from Tsang's work;¹⁷ this report also had included Tsang's study of C₂H₅Br. In summary, it appears that $10^{13.8} \exp(-54 \text{ kcal mol}^{-1}/RT)$ is a reasonable choice, if the upper range of values is weighted in anticipation that C₂H₅Br would resemble *t*-butyl bromide, if data from a wide range of temperature were available.

McGrath and Rowland¹⁴ used the QCISD method with the cc-pVDZ basis set to develop a model for HBr elimination from C_2H_5Br . Their calculated E_0 was 57.1 kcal mol⁻¹; the corresponding activation energy would be \approx 59 kcal mol⁻¹, which certainly is too high. The pre-exponential factor in Arrhenius form at 800 K from their model with the torsion treated as a hindered internal rotation is $15 \times 10^{13} \text{ s}^{-1}$, which is two times larger than the experimental upper limit $(6.3 \times 10^{13} \text{ s}^{-1})$ selected above. Our model for the C2H5Br reaction from the DFT calculations gives a similar pre-exponential factor of 13×10^{13} s^{-1} and $E_0 = 53.7$ kcal mol⁻¹. The results from the two different calculations confirm the general thesis that transition-state structures are not very sensitive to the computational method even though the calculated threshold energies may be significantly different. The possibility that the entropy of the calculated structure of the transition states for HBr elimination may be too large remains a question to be resolved.

The experimental rate constant reported¹¹ for C₂H₅Br activated with 91 kcal mol⁻¹ of energy formed by recombination of CH₃ with CH₂Br radicals has considerable uncertainty. However, this rate constant, $6 \pm 3 \times 10^9$ s⁻¹, still can provide a useful check for the threshold energy. Calculations from our model for C₂H₅Br with the torsion treated as a hindered internal rotor gave $k_E = 9.6 \times 10^9$ and 7.3×10^9 s⁻¹ for $E_0 = 53$ and 54 kcal mol⁻¹, respectively. Thus, the chemical activation data are consistent with the threshold energy obtained from thermal activation. The extensive studies of Raff and co-workers³⁹ with theoretical models for the dynamics of vibrationally excited CH₂=CHBr should be mentioned. They found rapid internal energy relaxation, relative to the rate for 1,1-HBr elimination, although they argue that C-Br rupture is not a statistical process. Given the internal rotational mode present in C₂H₅Br and C₂H₄Br₂, rapid relaxation of the internal energy in these molecules can be accepted relative to the rates of HBr elimination.

The primary goal of the two thermal studies of C₂H₅Br mentioned above was to obtain information about vibrational energy transfer using CH₂DCH₂Br¹⁵ and CHD₂CD₂Br.¹⁶ By fitting the falloff data, $\langle \Delta E_d \rangle$ was assigned as $1100 \pm 100 \text{ cm}^{-1}$ for self-collisions by Jung et al.¹⁵ The very low pressure pyrolysis experiments gave $\langle \Delta E_d \rangle$ as 850 and 1300 cm⁻¹ for C₂H₄ and C₆H₆, respectively, as bath gases, which are the most similar to SF₆ and C₄F₁₀ that were studied. Similar $\langle \Delta E_d \rangle$ values were reported from studies with isopropyl bromide.³⁶ In their

review of 2001, Barker, Yoder, and King⁴⁰ favored a nearly linear relationship between $\langle \Delta E_d \rangle$ and the vibrational energy of the excited molecule. A modest inverse dependence of $\langle \Delta E_d \rangle$ on temperature is usually found, although there are examples with a more pronounced inverse dependence.⁴⁰ Based upon the information just cited and the lack of explicit studies of bromoethanes with 90 kcal mol⁻¹ of vibrational energy in collisions at room temperature, we will adopt results from studies of collisional deactivation of fluoroethanes⁴¹ and 1,2-dichloroethane^{20,21} to assign relative efficiencies for deactivation of C₂H₄Br₂* and C₂H₄BrCl*with SF₆ and C₄F₁₀. For our purposes, we only need the factor that converts the observed experimental rate constant to the unit deactivation rate constant, which is then matched to $k_{\langle E \rangle}$ to obtain E_0 .

C. Rate Constants and Threshold Energies for C₂H₄Br₂ and C₂H₄BrCl. As an additional test case for use of the symmetric-rotor approximation to evaluate the density of states for C₂H₄BrCl, the density of states for C₂H₄Br₂ from the direct count was compared to a calculation using a symmetric rotor with an average barrier height (7.6 kcal mol^{-1}). At 90 kcal mol^{-1} the symmetric-rotor approximation for the density was higher than the direct-count density by a factor of 1.19. A comparison also was made to the thermal partition-functions at 800 K; the symmetric-rotor approximation was higher than exact-count value by a factor of 1.7, and the symmetric-rotor approximation is not adequate for the partition-function. At 800 K the exactcount partition-function actually converges before levels above the highest barrier $(9.7 \text{ kcal mol}^{-1})$ are needed in the summation. Upon the basis of this comparison and even better correspondence¹⁰ for the density of states between the direct-count and symmetric-rotor approximation for C₂H₄F₂, C₂H₄Cl₂, and C_2H_4CIF , the rate constants for C_2H_4BrCl should be within 15% of a direct-count evaluation of the density of states.

The experimental rate constant for $C_2H_4Br_2$ of $1.5 \times 10^9 \text{ s}^{-1}$ requires $E_0(\text{HBr}) = 58 \text{ kcal mol}^{-1}$ to obtain a match with the calculated rate constant; see Table 1. This 4–5 kcal mol}^{-1} increase in E_0 , relative to that for C_2H_5Br is consistent with the $\approx 7 \text{ kcal mol}^{-1}$ difference between C_2H_5Cl and CH_2ClCH_2Cl . The calculated difference in threshold energies for C_2H_5Br and $C_2H_4Br_2$ is 3.8 kcal mol}^{-1} for the 6-31G(d',p') basis set and 4.7 kcal mol}^{-1} for the 6-311+G(2d,p) basis set.

The threshold energies required to match the calculated and experimental rate constants for HCl and HBr elimination from CH₂BrCH₂Cl are 60 and 58 kcal mol⁻¹, respectively. Since the ratio of the sums of states for the HBr to HCl transition states is only 1.06, the difference of a factor of 2 in the experimental rate constants can be obtained only with a higher E_0 for the HCl case. These values, which are higher than the E_0 values for C₂H₅Cl and C₂H₅Br, closely match the values for CH₂BrCH₂Br and CH₂ClCH₂Cl.¹⁰

If one overall rotational degree of freedom is converted to an active mode in the calculation of densities and sums of states in eq 6, the rate constants would be reduced by a factor of $\approx 1.5^{.10}$ This has the effect of reducing the assigned E_0 values by 1 kcal mol⁻¹. For this reason the lower range of values for E_0 were selected in Table 1. Given the combined experimental and computational uncertainties, the reliability of the assigned E_0 values is probably ± 3 kcal mol⁻¹; however, the difference between E_0 (HCl) and E_0 (HBr) in CH₂BrCH₂Cl should be more reliable.

D. Rate Constants and Threshold Energies for Cl-Br Interchange in CH₂BrCD₂Cl. The transition state for interchange has higher frequencies, smaller moments of inertia, and a reduced s^{\dagger} ($s^{\dagger} = 1$) relative to the transition states for HBr and HCl elimination. Thus, a lower (\approx 7 kcal mol⁻¹) E_0 is required for the interchange rate constant to obtain a value that is similar to the elimination rate constants. Based on the approximate fitting of the data in Figure 3, as summarized below, the interchange rate constant should be 8 ± 2 times larger than the rate constant for HBr elimination from CH₂ClCD₂Br. Such a value corresponds to a threshold-energy of \approx 43 kcal mol⁻¹ for Cl/Br interchange. The DFT calculated threshold energy was 41.8 kcal mol⁻¹. Rate constants are first assigned to CH₂BrCD₂Cl (k_{HCI} and k_{DBr}) and to CH₂ClCD₂Br (k_{HBr} and k_{DCI}) based on the calculations outlined below. These calculated isotope effects were applied to the experimental rate constants from C₂H₄ClBr to obtain rate constants to interpret the ratios in Figure 3.

The changes in zero-point energies for CH₂BrCD₂Cl and CH₂ClCD₂Br relative to CH₂BrCH₂Cl (E_0 (HCl) = 60 kcal mol⁻¹ and E_0 (HBr) = 58 kcal mol⁻¹) gave values (kcal mol⁻¹) of 60.2 for loss of HCl and 59.1 for loss of DBr from CH₂BrCD₂Cl and 61.1 (DCl) and 58.2 (HBr) for CH₂ClCD₂Br. Combining these values with the sums and densities of states gave rate constants (10⁹ s⁻¹) of 0.34 for HCl and 0.49 for DBr for CH₂BrCD₂Cl and 0.23 for DCl and 0.74 for HBr for CH₂ClCD₂Br at 91 kcal mol⁻¹ of energy. These values correspond to kinetic-isotope effects of 2.1 for DCl and DBr processes and 1.5 for HCl and HBr processes. The threshold energy for interchange in CH₂BrCD₂Cl was unchanged relative to CH₂BrCH₂Cl, but the interchange rate constant decreased by a factor of 1.3 from the secondary kinetic-isotope effect.

The data in Figure 3 for Cl/Br interchange can be evaluated by a steady-state analysis. Let $[CH_2BrCD_2Cl]$ be [A] and $[CH_2ClCD_2Br]$ be [B] with total elimination rate constants k^A and k^B and let k_I be the interchange rate constant. In the limit of low pressure the steady-state equations are given below with *R* being the rate of recombination of CH₂Br and CD₂Cl.

$$d[A]/dt = 0 = R + [B]k_{I} - [A](k_{I} + k^{A})$$
 (7a)

$$d[B]/dt = 0 = k_{I}[A] - [B](k_{I} + k^{B})$$
 (7b)

Equation 7b gives the ratio of steady-state concentrations of A and B, eq 8, from which the ratio of HCl/DCl and HBr/DBr can be obtained as $k_{\text{HCl}}^{\text{A}}[A]/k_{\text{DCl}}^{\text{B}}[B]$ and $k_{\text{HBr}}^{\text{B}}[B]/k_{\text{DBr}}^{\text{A}}[A]$.

$$[A]/[B] = (k_{\rm I} + k^{\rm B})/k_{\rm I}$$
(8)

If $k_{\rm I} = 8k_{\rm HBr}^{\rm B}$, the product ratios are HCl/DCl = 1.60 and HBr/ DBr = 1.20. The ratios are 1.68 and 1.14, if $k_{\rm I} = 6k_{\rm HBr}^{\rm B}$. The experimental data at low pressure in Figure 3 are in agreement with such values for $k_{\rm I}$. The calculated rate constant for interchange is 5.4 and 8.6 times larger than $k_{\rm HBr}$ for thresholdenergies of 45 and 43 kcal mol⁻¹, respectively. If the collision rate becomes comparable to $k^{\rm B}$, then that term must be added to the numerator of eq 8 and the ratio of [A]/[B] becomes larger, and the HCl/DCl and HBr/DBr ratios increase and decrease, respectively. The experimental ratios are nearly constant, except possibly at the highest pressure (60 torr), and $k_{\rm I}$ must be 6–10 times larger than $k_{\rm HBr}^{\rm B}$.

V. Discussion

A. Cl/Br Interchange Reaction. The deuterium labeling experiment conclusively demonstrated that the Br-Cl interchange reaction is faster than HBr and HCl elimination reactions from CH₂ClCH₂Br molecules with an energy of 91 kcal mol⁻¹. In fact, the threshold energy for interchange is 15 kcal mol^{-1} lower than for the elimination reactions, and interchange is the dominant reaction. The E₀ for Cl/F interchange for CH₂FCH₂Cl also is the lowest threshold energy, based on computational results;¹⁰ however, 1,2-HCl and 1,2-HF elimination would be competitive for CH₂ClCH₂F. Since the threshold energy for 1,2-HX elimination is elevated when halogen atoms are on adjacent carbon atoms, the 1,2-dihaloethane molecules provide some of the best systems to demonstrate halogen exchange reactions. We have previously shown¹⁰ that the threshold energy for 1,1-HX elimination in 1,2-dihaloethanes is between 80-90 kcal mol⁻¹; thus, a mechanism involving 1,1-HX elimination followed by H migration need not be considered. The entropies of the HBr and HCl transition states are very similar, as demonstrated by the ratios (at the same energy) of their sums of vibrational states, which is only 1.06 in favor of the transition state for HBr elimination. In contrast, the ratio of the sums of states for the HBr versus the Br/Cl interchange transition states is 2.3, and the interchange transition state has the smaller entropy. The three transition-state structures from CH₂ClCH₂Br are shown in Figure 4. One common feature is the trigonal planar geometry for the carbon atoms in the interchange transition state and the carbon atom from which the chlorine or bromine atom is departing in the elimination transition states. The positions of the bromine and chlorine atoms in the interchange transition state are nearly the same, which seems surprising, but such a structure is consistent with the similar atomic radii of the two atoms, which differ by only 15%. This similarity can be contrasted to the difference between the positions of fluorine and chlorine atoms in the Cl/F interchange transition state of CH₂ClCH₂F, which also is shown in Figure 4. The C-Cl distance is the same as for the Cl/Br case, but the C-F distance is much shorter. According to the calculations, the E_0 for Cl/F interchange in CH₂ClCH₂F is 60 kcal mol⁻¹ and that for Br/F interchange in CH₂BrCH₂F is 57 kcal mol⁻¹. These are much larger than 43 kcal mol⁻¹ for CH₂BrCH₂Cl. Exploratory calculations also were done for CH₃CHClCH₂Br; the calculated E_0 for interchange was 3 kcal mol⁻¹ lower than for CH₂ClCH₂Br, and Cl/Br interchange should be expected whenever a bromine atom and a chlorine atom are on adjacent carbon atoms in chlorobromoalkanes.

In an effort to understand the nature of the interchange transition states and the difference between Br/Cl and Cl/F or Br/F cases, the charges on the atoms in the structures were examined using the atoms-in-molecules approach.42 The charges on the atoms of the transition state for Cl/Br interchange are Cl(-0.40), Br(-0.28), C(+0.089), and H(+0.13). The carbon atoms become more positive in the transition state for Cl/F interchange; F(-0.49), Cl(-0.44), C(+0.23), and H(+0.12). The positive H₂C-CH₂ backbone is surrounded by the negative halogen atoms. We did not do calculations that would provide information about the molecular orbitals. However, an attractive intuitive description is Π -type bonding involving the p-orbitals of the carbon atoms and the halogen atoms. The lines drawn in Figure 4 between the carbon atoms and the halogen atoms denote distances and not necessarily localized chemical bonds. The reaction coordinate for the interchange is simply a twisting (torsional) motion of the H_2C-CH_2 plane bringing each CH_2 group closer to the stationary halogen atoms. An Intrinsic Reaction Coordinate calculation confirms the conversion between CH2BrCD2Cl and CH2ClCD2Br via the interchange transition state in Figure 4.



Figure 4. Transition states computed from the B3PW91/6-31G(d',p') method for the three reactions of CH₂BrCH₂Cl. The diagram for Cl/F interchange from CH₂ClCH₂F is included for comparison. The similar distance of the Br and Cl atoms from the plane gives a very symmetric structure, and the planar structure for the CH₂CH₂ backbone of the interchange transition states should be noted. The Cl–Br interchange transition state forms by twisting of the CH₂–CH₂ backbone between the immobile Br and Cl atoms whose separation in the *anti* configuration of the molecule (4.48 Å) and in the transition state (4.45 Å) remains constant. The degree of planarity of the two carbons is identified by the angle between the extension of the C–C axis and the plane defined by the three atoms, e.g. CH₂, CHCl, or CHBr. As points of reference, 55 and 0° correspond to 100% tetrahedral and trigonal planar, respectively. The lines drawn from the halogen atoms to the carbon atoms are convenient ways to denote the distances; they do not necessarily denote chemical bonds; see text.

B. Comparison of Elimination Reactions for CH₂XCH₂Y Molecules. As already noted, the $\Sigma P^{\dagger}(E - E_0)$ of the transition states for HCl and HBr elimination from CH₂BrCH₂Cl are very similar. The calculated structures for the transition states also are very similar as illustrated by the diagrams shown in Figure 4. The long C–Cl and C–Br distances and the nearly planar geometry around the H₂C_x end of the transition states are especially noteworthy. The calculated pre-exponential factors for both HCl and HBr elimination tend to be a factor of ≈ 2 larger than the experimental results as demonstrated here by the comparison with C₂H₅Br and by other comparisons for various alkyl chlorides.^{10,12,43} The discrepancy with the experimental results is a consequence of the long C–Cl and C–Br distances, which introduce low frequency vibrations into the

model of the transition states. Different levels of theory and different theoretical approaches give similar transition-state structures. Although this discrepancy is not very serious for most aspects associated with HCl and HBr unimolecular elimination reactions, the long C–Cl and C–Br distances in the transition states remain an interesting question.

Except for CH₂BrCH₂F, the experimental data for all CH₂XCH₂Y(X,Y = Br, Cl, F) type molecules have been analyzed recently. In every case the threshold-energy is several kcal mol⁻¹ higher than for the C₂H₅X molecule. Furthermore, $E_0(HX)$ tends to be the similar to $E_0(HY)$, although $E_0(HCl)$ is 2 kcal mol⁻¹ higher than $E_0(HBr)$. One possible explanation for the elevation of E_0 is the net reduced sum of the bond energies for the HXC_H end of the transition state relative to the

 H_2C_H end of C_2H_5X , where the H subscript denotes the carbon atom attached to the departing H atom. The calculated E_0 values for CH₂BrCH₂Br and CH₂BrCH₂Cl were very close to the experimentally assigned values. Therefore, we also calculated the E_0 for HBr and HF elimination from CH₂BrCH₂F to complete the series, and the values are 57.5 and 60.6, respectively. The 3 kcal mol⁻¹ difference is consistent with the limited experimental data, which indicate that the HBr elimination rate is faster than the HF elimination rate.^{44–46} The possibility of Cl/Br, F/Cl, and F/Br interchange should be remembered when considering the proposed reaction mechanisms for infraredmultiphoton excitation of haloethanes.^{47–50}

VI. Conclusions

The facile interchange of bromine and chlorine atoms located on adjacent carbon atoms has been demonstrated by observation of CH₂ClCD₂Br formation from vibrationally excited CH₂BrCD₂Cl molecules that were generated by the recombination of CH₂Br and CD₂Cl radicals at room temperature. The vinyl halide product ratios for loss of HCl/DCl and HBr/DBr from CH₂BrCD₂Cl and CH₂ClCD₂Br were used to identify the interchange reaction, which is 8 ± 2 times faster than the elimination reactions. This information was combined with observation of the HBr and HCl elimination reactions from CH2BrCH2Br and CH2BrCH2Cl formed by radical combination to assign threshold energies of 60 kcal mol⁻¹ for HCl elimination, 58 kcal mol⁻¹ for HBr elimination and \simeq 43 kcal mol⁻¹ for Cl/Br interchange. These assignments are in good accord with the threshold energies calculated from DFT with the B3PW 91/6-31G(d',p') method. The low threshold energy for Br/Cl interchange suggests that this unimolecular process should be expected whenever chlorine and bromine atoms are located on adjacent carbon atoms in chlorobromoalkyl species. The transition state for Br/Cl interchange is very symmetric with the Br and Cl atoms resting equidistant between the carbon atoms just above and below the plane of the H₂C-CH₂ structure. According to the DFT calculations, the E_0 for interchange of fluorine and chlorine atoms in CH2FCH2Cl and fluorine and bromine atoms in CH₂FCH₂Br are 60 and 57 kcal mol⁻¹, respectively. Based on comparison to data from the C₂H₅Br reaction, the transition state calculated by DFT with the B3PW91/6-31G(d',p') method for HBr elimination should be as reliable as that for HCl elimination reactions. In fact, the transition states for HCl and HBr elimination are very similar. The threshold energies for CH2BrCH2Br and CH2ClCH2Br assigned here follow the general trend of elevated threshold energies for 1,2dihaloethanes, relative to the corresponding ethyl halides.

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Supporting Information Available: Tables of the molecular and transition state structure vibrational frequencies, atomic charges, overall moments of inertia, and the reduced moments of inertia for the internal rotors calculated using B3PW91/6-31G(d',p') for CH₂BrCH₂Cl, CH₂BrCD₂Cl, and CH₂ClCD₂Br. This information is available free of charge via the Internet at http://pubs.acs.org.

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