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Collisional Energy Transfer in the Two-Channel Thermal Unimolecular Reaction of Bromoethane-2-d

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Unimolecular thermal decomposition in the two-channel bromoethane-2-*d* system was studied over the temperature range of 660-706 K in the presence of CF₄ and He bath gases. The C₂H₅Br system was also studied as a reference process. The average energy removed per collision from energized bromoethane-2-*d* by a bath gas $(\Delta E)_{down}$ is as follows: by the substrate, 1100 cm⁻¹ (stepladder model); by CF₄, 675 cm⁻¹ (exponential model, EXP); by He, 215 cm⁻¹ (EXP). Comparison is made with recent studies of direct measurements. The relative rate ratio of two-channel reaction has been expressed in terms of microscopic rate ratio and distribution function of the reacting molecule. Arrhenius parameters, i.e., log *A* and *E_a* (kcal/mol), at ca. 50 Torr of total pressure were found to be as follows: for C₂H₅Br, 13.37 ± 0.18, 53.36 ± 0.55; for CH₂DCH₂Br, 13.16 ± 0.16 and 53.30 ± 0.51 (HBr elimination) and 12.83 ± 0.30 and 54.29 ± 0.92 (DBr elimination).

I. Introduction

The multichannel thermal unimolecular reaction systems have attracted considerable interest in elucidating more reliable and significant information about intermolecular energy-transfer process in thermal reactions. The measurements of the ratio of rate constants of competitive reactions have canceling effects of unpredictable experimental error and produces a marked difference between weak and strong collision systems at low pressures. Since the usefulness was first recognized by Chow and Wilson,¹ successful utilizations of two-channel systems have been demonstrated for the isomerization of cyclopropane-1, $1-d_2$ in He bath gas systems² and for the decompositions³ of C₃H₇I, CH₂DCH₂Cl, and CHD_2CD_2Br at very low pressure. The work extended to the three-channel system of cyclopropane-1-t-2,2- d_2 by Rabinovitch et al.⁴ has shown a rather marked decline of both the relative collision efficiency, β_w , and the average energy removed per collision, $\langle \Delta E \rangle_{\text{down}}$, for several bath gases with temperature rise. These indirect measurements of the collisional energy-transfer parameters require the explicit knowledge of kinetic parameters of reference process, while recent direct measurements⁵ by transient spectroscopy do not employ the unimolecular reaction system. However, an accurate evaluation of the microscopic rate constant k(E) and critical energy E_0 of the unimolecular reaction from thermal or external activation study renders it possible to obtain more reliable information on energy transfer.

In the present study, intermolecular energy transfer has been investigated in two-channel competitive HBr/DBr elimination reactions of CH_2DCH_2Br . The experiments have been carried out both in the neat system and in the presence of He and CF_4 as collisional partners. The energy-transfer parameters of weak colliders He or CF_4 have been deduced from differential dilution experiments by collision partners at constant pressure of parent gas. Concomitant work on thermal reaction of C_2H_5Br has been used to determine the rate constant parameters for CH_2DCH_2Br and to obtain supplementary information on vibrational energy transfer of neat system.

Measurement of the relative rate ratio as a function of pressure in H(D)Br elimination reactions of CH_2DCH_2Br has permitted the reliable evaluation of intermolecular energy-transfer parameters. We have presented an explicit expression for the macroscopic rate ratio of two-channel reaction in terms of the energydependent microscopic rate ratio and the normalized distribution function of reacting molecule dissociating into each reaction path. This approach has permitted a useful interpretation on the pressure dependence of the relative rate ratio in weak and strong collision systems of thermal unimolecular reaction.

II. Experimental Section

The experiment was performed in a static system with a 887.0-cm³ (65 mm i.d. \times 30 cm length) cylindrical quartz vessel, which had been seasoned by a number of runs at higher pressure and temperature than the actual run prior to the experiment. The reaction vessel was placed in the middle zone of the tubular furnace, Electroglass, equipped with three separated heating zones. The temperature of the furnace was controlled by internal thermocouples within ± 1 °C along the length of the furnace. The fluctuation of temperature in the reaction vessel was kept less than ± 0.5 °C throughout the entire experiment. The dead volume of the reaction was less than 1% of the total volume.

The reaction product analysis was carried out with a two-stage gas chromatograph equipped with a single flame ionization detector (FID). The first stage high temperature column, 1/3 m length $\times 1/8$ in. o.d. stainless steel Porapak S, was operated at 80 °C to separate the reaction product from the reactant. The reaction product portion from the first stage separation was then

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introduced into the second stage, a 30 m length (100 ft) $\times 1/8$ in. o.d. stainless steel AgNO₃/ethylene glycol column.⁶ Quantitative analysis of the product olefins, i.e., CH₂CH₂ and CHD-CH₂, was carried out by comparison of the chromatograms to those of the authentic samples.

CH₂DCH₂Br and CHDCH₂, Merck-Sharpe & Dohme Co., stated isotopic purity of 98%, were purified by the freezepump-thaw method and used without any further isotope purification. CH_2CH_2 and CF_4 , stated purity of 99.5%, Matheson Co., were also purified by the same technique. He used as a collision partner was Matheson research grade, 99.9999%.

III. Calculations

Master Equation. The master equation which describes the time history of populations, n_i , of the molecule at energy level i can be written as eq 1 for the thermal unimolecular reaction,⁷

$$dn_i/dt = f_i + \omega \sum_j p_{ij} n_j - \omega n_i - k_i n_i$$
(1)

where p_{ii} is the collisional transition probability of the reactant molecule from energy level j to i and must satisfy the condition of completeness and detailed balance, k_i the microscopic rate constant at the *i*-th energy state, ω the collisional frequency, and f_i the rate of an external input into the *i*-th level.

The numerical solution of eq 1 in the steady state was obtained by the iteration method utilizing Tardy and Rabinovitch's algorithm.⁸ For the steady-state populations, n_i^{ss} , the modified transition probabilities with the *i*-th column normalized to $\omega/(\omega)$ $(+ k_i)$ operated repeatedly on a given population distribution until the population output unchanged. Then, the macroscopic rate constant, k_{uni} , was calculated from

$$k_{\rm uni} = \sum k_i n_i^{\rm ss} / \sum n_i^{\rm ss}$$
(2)

Since the collisional up-transition probability, p_{ij} (i > j), can be obtained by applying the detailed balance requirements to the down-transition probability, all elements of p_{ii} were calculated by considering only the down-transition probability. For a chosen model, the adjustable parameter used in fitting the experimental results is the average energy removed per collision, $\langle \Delta E \rangle_{\text{down}}$. Together with the functional form of p_{ij} 's, $\langle \Delta E \rangle_{down}$ is one of the most significant pieces of information about collisional energy transfer at highly excited energy level. The energy-transfer models used in the present work were stepladder (SL) for the strong collider and exponential (EXP) model for the weak collider.

Isotopic Rate Constant Ratio. The microscopic rate constants in eq 1 were calculated from the RRKM expression.⁹ For the calculation, the sums, G(E), and the densities, N(E), of eigenstates were evaluated by direct counting using Beyer-Swinehart algorithm¹⁰ extended by Stein et al.¹¹ The extended computation permitted to calculate G(E), N(E), and the partition functions for harmonic oscillators with the hindered internal rotor. The torsional modes of CH₂DCH₂Br were treated as the true hindered internal rotors.¹² The remaining vibrational modes for molecule and complexes were treated as harmonic oscillators assuming adiabatic overall rotations.

Since the microscopic rate constant of the competitive reaction at the *i*-th energy level is the sum of the rate constants of all

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TABLE I: Vibrational Frequencies and Moments of Inertia for **Molecules and Activated Complexes**

molecules	vibrnl freq, cm ⁻¹	moments of inertia, amu·Å ²
CH₃CH₂Br	3020, 2985, 2975, 2963, 2927, 1456, 1446, 1446, 1380, 1244, 1185, 1065, 1023, 960, 780, 562, 294	143.3, 132.8, 16.83, 2.865 ^a
complex for HBr elimination	3035, 2997, 2963, 2934, 1604, 1561, 1243, 1208, 1107, 1048, 1009, 984, 904, 822, 631, 397, 343	113.7, 87.95, 32.62
CH ₂ DCH ₂ Br	3020, 2977, 2969, 2947, 2188, 1460, 1407, 1293, 1272, 1226, 1176, 1022, 951, 892, 727, 559, 283	148.8, 137.9, 18.62, 3.705 ^a
complex for HBr elimination	3035, 2970, 2959, 2196, 1580, 1446, 1227, 1109, 1087, 1009, 991, 870, 814, 797, 629, 394, 380	119.4, 91.73, 36.30
complex for DBr elimination	3035, 2997, 2963, 2934, 1604, 1561, 1242, 1195, 1052, 1036, 1007, 977, 873, 656, 573, 376, 270	116.4, 88.01, 35.24

^a The reduced moments of inertia of the internal rotor necessary for calculating the hindered rotational eigenvalues of molecules.

reaction channels, the total microscopic rate constant for CH₂D-CH₂Br is given by $k(E_i) = k^{H}(E_i) + k^{D}(E_i)$, where $k^{H}(E_i)$ and $k^{D}(E_{i})$ are the microscopic rate constants of HBr and DBr elimination reactions at the *i*-th level, respectively. The steady-state populations depeleted by two-channel reactions were determined by the numerical solution of eq 1, and the isotopic rate constant ratio of HBr to DBr elimination is given by

$$k_{\rm uni}{}^{\rm H}/k_{\rm uni}{}^{\rm D} = \sum_{E_0}{}^{\rm H}k^{\rm H}(E_i)n_i{}^{\rm ss}/\sum_{E_0}{}^{\rm b}k^{\rm D}(E_i)n_i{}^{\rm ss}$$
(3)

where E_0^{H} and E_0^{D} are the critical energies for HBr and DBr elimination processes, respectively.

Rotational and Vibrational Analysis. The fundamental frequencies for C_2H_5Br were obtained from the available spectroscopic data,¹³ and the potential barrier for the hindered internal rotor of CH₃ group were taken from the literature values.¹⁵ The frequencies for CH₂DCH₂Br were assigned from the normalcoordinate analysis utilizing Wilson's FG matrix method¹⁴ with transferred valence force field from bromoethane- d_0 , $-d_2$, $-d_3$, and $-d_5$.¹³ The moments of inertia for the molecules were calculated from the known geometry of the molecule.¹⁵

The planar four-centered complex models were adopted for the geometry of the activated complex which were suggested for similar systems on the basis of experiments¹⁸ and MO calculations.16,17

The bond order of the complex was varied such that the model chosen reproduced the experimental Arrhenius parameters as same manner as Setser's suggestion.¹⁸ The imaginary frequency associated with the reaction coordinate was obtained by assigning a negative H(D)Br stretching force constant in a similar manner as for the complex model calculation by Tschuikow-Roux et al.¹⁹ Using the force constant-bond order relationship²⁰ for the

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⁽¹²⁾ For the calculation of true hindered internal rotation, the eigenvalues were evaluated in two energy ranges separately, i.e., $E < 3V_0$ by solving the real symmetric Hamiltonian matrices (ref 31) representing the hindered internal rotor and $E < 3V_0$ range by applying the second-order perturbation method to the Hamiltonian equation (cf. ref 32).

TABLE II: Collision Parameters

molecules	$\sigma_{\rm d},{\rm \AA}$	$\epsilon/k_{\rm B}(T)$	μ _d , D
CH ₃ CH ₂ Br ^a	4.70	452	2.03
He	2.55	10	0.0
CF_4	4.49	167	0.0

"The collision parameters of CH2DCH2Br were taken to be the same values as for CH₃CH₂Br.

stretching mode of the four-membered ring, the frequencies for the complex were calculated by the FG-matrix treatment with remaining force constants taken as the same values as the molecule, except the torsional mode. Two restrictions were imposed on the variation of bond orders and the adjustment of the ring frequency to obtain the best fit to experimental data and to satisfy simultaneously the product rule within 8%. The well-refined bond orders for C-C, C-Br, C-H, and H-Br bonds were finally determined to be 1.6, 0.9, 0.1, and 0.1, respectively, which are very similar to those of the Setser's revised model.²¹ The assigned frequencies and moments of inertia for the molecule and the activated complexes are summarized in Table I. The reaction path degeneracies for HBr and DBr elimination processes of CH₂DCH₂Br were taken as $^4/_3$ and $^2/_3$, respectively, and 2 for the CH₃CH₂Br reaction system. The critical energies for HBr and DBr eliminations of CH₂DCH₂Br were evaluated to be 52.96 and 54.13 kcal/mol, respectively, and 52.88 kcal/mol for the reaction of CH₃CH₂Br.

Collisional Frequencies. For the analysis of the experimental results by eq 1 the collision parameters were calculated by using the intermolecular potentials appropriate for colliding pairs. For nonpolar gases, the collision frequency is based on Lennard-Jones²² and Stockmeyer potentials²³ for polar gases. The collision number was calculated by using the reduced mass of the reacting molecule A and the bath gas M, μ_{AM} , the collision diameter σ_d , and the reduced collision integral $\Omega^{(2,2)*}$. The $\Omega^{(2,2)*}$ for two different potentials were given by the approximate equations²³

 $\Omega^{(2,2)*}(\text{Lennard-Jones}) =$ $A/T^{*B} + C/\exp(DT^*) + E/\exp(FT^*)$ $\Omega^{(2,2)*}(\text{Stockmeyer}) = \Omega^{(2,2)*}(\text{Lennard-Jones}) + 0.2\delta_p^2/T^*$ (4)

where $T^* = k_{\rm B}T/\epsilon$, ϵ being the potential well depth, A = 1.16145, B = 0.14874, C = 0.52487, D = 0.77320, E = 2.16178, F =2.43787, and the dimensionless polar parameter $\delta_p = \mu_d^2/2\epsilon\sigma_d^3$, μ_d being the dipole moment. In the case of different colliding species, the collision parameters were obtained by the combination

rules, $\sigma_{d,AM} = (\sigma_{d,AA} + \sigma_{d,MM})/2$ and $\epsilon_{AM} = (\epsilon_{AA}\epsilon_{MM})^{1/2}$. The parameters for polar parent molecule were determined by the correlation method of Stiel and Thodes²⁴

$$\sigma_{\rm d} = 0.785 V_{\rm c}^{1/3}; \quad \epsilon/k_{\rm B} = 0.897 T_{\rm c} \tag{5}$$

where V_c is the critical molar volume (cm³/mol) and T_c the critical temperature (K). The Lennard-Jones parameters of He and CF4 were taken from the literature.^{22,24} The parameters used in this work are summarized in Table II.

IV. Results

The collisional activation reactions of C₂H₅Br and CH₂DCH₂Br have been investigated at temperatures between 636 and 730 K and at constant pressures of about 50 Torr. Arrhenius parameters for these reactions are found to be log $A = 13.37 \pm 0.18$ and E_a = 53.36 ± 0.55 kcal/mol for CH₃CH₂Br; log A = $13.16 \oplus 0.16$ and $E_a = 53.53 \pm 0.51$ kcal/mol for HBr elimination of CH₂D- CH_2Br ; log $A = 12.83 \pm 0.30$ and $E_a = 54.29 \pm 0.92$ kcal/mol for DBr elimination of CH₂DCH₂Br. The high-pressure limit rate



Figure 1. Pressure dependence of unimolecular rate constants for CH_2DCH_2Br (\bullet) at 706.4 K and CH_3CH_2Br (\blacksquare) at 693.2 K, and the calculated values (---) for SL with $\langle \Delta E \rangle_{down} = 1050 \text{ cm}^{-1} (CH_2DCH_2Br)$, and 1200 cm⁻¹ (CH₃CH₂Br). For clarity, data and curve for CH₃CH₂Br are displayed downward.

TABLE III: $\langle \Delta E \rangle_{down}$ (cm⁻¹) of the CH₂DCH₂Br Systems^a

		<i>Т</i> , К			
collision partners	model	706.4	693.2	660.2	
CH ₂ DCH ₂ Br	SL	1050	1200	1100	
CF₄	SL	625	675	650	
	EXP	650	700	675	
He	SL	250	265	270	
	EXP	200	215	220	

^a Uncertainties in $\langle \Delta E \rangle_{down}$ are ca. 10%.

constants, k_{uni} , were obtained by plotting the first-order rate constants against the reciprocal of the reactant pressure²⁵ at each temperature and they were found to be $\log A_{\infty} = 13.62 \pm 0.22$ and $E_{a,\infty} = 54.02 \pm 0.71$ kcal/mol for CH₃CH₂Br and were in good agreement with the reported values, e.g., $E_{a,\infty} = 53.7$ kcal/mol and log $A_{\infty} = 13.19$ by Tsang,²⁶ and $E_{a,\infty} = 53.9$ kcal/mol and log $A_{\infty} = 13.45$ by Thomas.²⁷ The high-pressure limit Arrhenius parameters for CH2DCH2Br were found to be $\log A_{\infty} = 13.35 \pm 0.17$ and $E_{a,\infty} = 54.05 \pm 0.88$ for HBr elimination; $\log A_{\infty} = 13.18 \pm 0.31$ and $E_{a,\infty} = 55.28 \pm 0.92$ for DBr elimination reactions.

The pressure dependences of the rate constants for CH₃CH₂Br and CH₂DCH₃Br systems were studied in the fall-off region at three temperatures, 660.2, 693.2, and 706.4 K. The experimental fall-off plots, $\log k_{uni}/k_{uni}^{\infty}$ vs. log P, for the reaction are displayed in Figure 1 together with the theoretical curves (solid line) calculated by the numerical solution of eq 1 in the steady state. The pressure dependence on the isotopic rate ratio for two-channel reactions of CH₂DCH₂Br was also studied in the fall-off region at various pressures of He and CF_4 in attempts to get information on the weak collision effect and the collisional energy transfer. The dilution change was made from 0 to 240 Torr with the constant substrate pressure at 0.178 ± 0.003 Torr. Typical experimental results of the intramolecular isotope effect, eq 3, at

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Figure 2. Pressure dependence of the isotopic rate ratio for CH₂DCH₂Br at 706.4 K: (•) the substrate; (•) CF₄; (•) He collision partners; (--) the calculated curve for the substrate (SL), CF₄ (EXP), and He (EXP) with $\langle \Delta E \rangle_{down} = 1050, 650, and 200 \text{ cm}^{-1}$, respectively.

706.4 K are presented in Figure 2, with theoretical curves for the best-fitted values of $\langle \Delta E \rangle_{down}$. The intramolecular isotope effect of the CH₂DCH₂Br system is enhanced with pressure reduction. The best-estimated $\langle \Delta E \rangle_{down}$ of the collision partners and neat substrate at three temperatures are given in Table III for SL and EXP models. It is worth pointing out that the $\langle \Delta E \rangle_{down}$ value for EXP model is less than that for the SL model when He is used as the collision partner while the trend is opposite when the step size of the collider is increased. This cross-over phenomenon is in agreement with the behavior predicted by Tardy and Rabinovitch.⁸

V. Discussion

Pressure Dependence of Relative Rate Ratio in Two-channel Thermal Unimolecular Reaction. The relative macroscopic rate of two modes can be expressed in terms of microscopic properties by factorizing into two parts

$$k_{uni}^{H} / k_{uni}^{D} = k_{uni}^{1} / k_{uni}^{u} = \sum_{E_{0}^{i}} k_{i}^{1} n_{i}^{ss} / \sum_{E_{0}^{u}} k_{i}^{u} n_{i}^{ss}$$

$$= \left[\sum_{E_{0}^{u}} k_{i}^{1} n_{i}^{ss} / \sum_{E_{0}^{u}} k_{i}^{u} n_{i}^{ss} \right] \left[\sum_{E_{0}^{i}} k_{i}^{1} n_{i}^{ss} / (\sum_{E_{0}^{i}} k_{i}^{1} n_{i}^{ss} - \sum_{E_{0}^{i}} k_{i}^{1} n_{i}^{ss}) \right]$$

$$= \left[\sum_{E_{0}^{u}} k_{i}^{1} n_{i}^{ss} / \sum_{E_{0}^{u}} k_{i}^{u} n_{i}^{ss} \right] \left[1 / (1 - \sum_{E_{0}^{i}} k_{i}^{1} n_{i}^{ss} / \sum_{E_{0}^{i}} k_{i}^{1} n_{i}^{ss}) \right]$$

$$= \mathbb{E} [1 / (1 - \Theta)] = \mathbb{E} \cdot \Phi \qquad (6)$$

where

$$\Xi = \sum_{E_0^u} k_i^{\,l} n_i^{\,ss} / \sum_{E_0^u} k_i^{\,u} n_i^{\,ss}$$
$$\Theta = \sum_{E_0^{\,l}} k_i^{\,l} n_i^{\,ss} / \sum_{E_0^{\,l}} k_i^{\,l} n_i^{\,ss}, \quad \Phi = 1/(1-\Theta)$$

and the index l and u denote the lower and the upper reaction modes with respect to their critical energies, respectively. For simplicity, let us define a normalized distribution function R_i by

$$R_{i} = k_{i}^{u} n_{i}^{ss} / \sum_{E_{0}^{u}} k_{i}^{u} n_{i}^{ss} = k_{i}^{u} (n_{i}^{ss} / n_{tot}^{ss}) / k_{uni}^{u}$$
(7)

where $n_{\text{tot}}^{ss} = \sum n_i^{ss}$. Then the first factor, Ξ , in eq 6 becomes

$$\Xi = \sum_{E_0^u} k_i n_i^{ss} / \sum_{E_0^u} k_i^u n_i^{ss} \\
= \sum_{E_0^u} (k_i^1 / k_i^u) k_i^u n_i^{ss} / \sum_{E_0^u} k_i^u n_i^{ss} = \langle k_i^1 / k_i^u \rangle_R$$
(8)

From eq 8, Ξ describes an average microscopic rate ratio over R_i which represents the normalized steady-state distribution of

TABLE IV: Calculated Pressure Dependence of Ξ and Φ Factors in Eq 6 for Two-Channel Decompositions of $CH_2DCH_2Br^a$

collision freq, s ⁻¹	$k_{\rm uni}^{\rm H}/k_{\rm uni}^{\rm D}$	Ξ	Φ	
6.460×10^{8}	3.649	3.487	1.033	
2.043×10^{8}	3.715	3.584	1.037	
6.460×10^{7}	3.830	3.680	1.041	
2.043×10^{7}	4.016	3.829	1.049	
6.460×10^{6}	4.297	4.042	1.063	
2.043×10^{6}	4.712	4.328	1.089	
1.149×10^{6}	4.986	4.497	1.109	
6.460×10^{5}	5.320	4.683	1.136	
2.049×10^{4}	6.217	5.074	1.225	

^a For the stepladder model of collisional transition probability with $\langle \Delta E \rangle_{down} = 1050 \text{ cm}^{-1}$.

the excited molecules dissociating into the upper reaction channel per unit time. The θ in the second part of Φ represents the fractional contribution of the lower channel reaction (vide infra).

Utilizing Forst's formulation²⁸ of the microscopic rate constant, $k(E_i) = A_{\infty}N(E_i - E_{a,\infty})/N(E_i)$ which was derived by mathematical deconvolution process on A_{∞} and $E_{a,\infty}$, we can obtain a general expression for the energy dependence of $k^{l}(E_i)/k^{u}(E_i)$. If the density of states of the molecule is evaluated by Whitten-Rabinovitch approximation, the best estimated critical energy is E_0 = $E_{a,\infty}$ and $\Delta E_0 \ll E_z$ (zero-point energy), the rate ratio then is approximated by

$$k^{l}(E_{i})/k^{u}(E_{i}) = \frac{A_{\infty}^{l}N(E_{i} - E_{a,\infty}^{l})}{A_{\infty}^{u}N(E_{i} - E_{a,\infty}^{u})}$$

= $\{A_{\infty}^{l}/A_{\infty}^{u}\} \exp[(s-1)\Delta E_{0}/(E_{i}^{+} + a(E_{i}^{+}/E_{z})E_{z})]$ (9)

where s is the number of vibrational oscillators, E^+ the nonfixed energy given by $E_i^+ = E_i - E_0^u$, and $\{a(E_i^+/E_z)\}$ the unique function of a reduced energy E_i^+/E_z . Since the Whitten-Rabinovitch correction factor $\{a(E_i^+/E_z)\}$ is an increasing function of E_i^+/E_z , $k^1(E_i)/k^u(E_i)$ in eq 9 is monotonically decreased with increasing internal energy regardless of the physical nature of each reaction channel within Forst's approximate treatment for $k(E_i)$.

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In order to obtain the information on the pressure dependence of Ξ , the statistical characteristics of $R(E_i)$ at various collision rates have to be analyzed. At higher energy level, the decreasing rate of the steady-state distribution $k(E_i)n^{ss}(E_i)/n_{tot}^{ss}$ is faster than that of the normalization constant k_{uni}^{u} by collision rate reduction. Consequently $R(E_i)$ is decreased as collision rate decreases. However, at lower energy level above the threshold energy, the reverse trend occurs; i.e., $R(E_i)$ increases with collision rate reduction due to the smaller change of $k^{u}(E_{i})n^{ss}(E_{i})/n_{tot}^{ss}$ than that of k_{uni}^{u} . Therefore, by collision rate reduction, both the average energy $\langle E_u^+ \rangle$ possessed by reacting molecules of the upper channel and the energy E_{max}^+ at the maximum value of $R(E_i)$ decrease toward the low-pressure limit value. Consequently, the height of its maximum increases and the shape of $R(E_i)$ becomes sharpened as shown in Figure 3. Hence, the average value of $k^{l}(E_{i})/k^{u}(E_{i})$ over $R(E_{i})$ of the reacting molecule increases with pressure reduction as summarized in Table IV, since the larger value of $k^{l}(E_{i})/k^{u}(E_{i})$ at lower energy level is more severely effected by $R(E_i)$ than the smaller $k^{l}(E_i)/k^{u}(E_i)$ at higher energy level.

The term Θ in the second factor Φ denotes the partial integral of $R(E_i)$ of the lower channel in the range between the critical energies of two competitive channels

$$\Theta = \sum_{E_0^{i}}^{E_0^{u}} k^{l}(E_i) (n^{ss}(E_i) / n_{tot}^{ss}) / k_{uni}^{l} = \sum_{E_0^{i}}^{E_0^{u}} R^{l}(E_i)$$
(10)

From the discussion given above on the pressure dependence of the shape of $R(E_i)$ for the upper channel, the estimation of the pressure dependence of Φ is rather straightforward. Since the lower channel shows similar trends as the upper channel, it is

⁽²⁸⁾ Forst, W. J. Phys. Chem. 1972, 76, 342.



Figure 3. Calculated plots of R_i vs. E for CH₂DCH₂Br at the collision rates of 6.46 × 10⁵ (--) and 6.46 × 10¹⁰ (---), and k_i^1/k_i^u (..-.). The calculated values of R_i correspond to the SL model with $\langle \Delta E \rangle_{down} = 1050$ cm⁻¹ at 706.4 K. The energy scale is given with E_0^D as zero of reference.

readily seen that the partial summation value Θ increases as the collision rate decreases, and thus Φ in eq 6 also increases as tabulated in Table IV.

From the foregoing discussion, the relative macroscopic rate ratio in the two-channel reaction is increased with pressure reduction. By factorizing the rate ratio into two parts, a useful interpretation of the pressure dependence of rate ratio is made successfully in terms of the energy-dependent microscopic rate ratio and $R(E_i)$ of the reacting molecule dissociating into each reaction channel per unit time. It is also readily recognized that the two-channel reaction system can be extended to the multichannel system by making combinations of pairs of reaction channels.

Weak Collision Effects on Relative Rate Ratio. The Lindemann assumption of a strong collision denotes unit efficiency for the collisional deactivation of all reactive molecules above the critical energy. And the steady-state distribution of excited states for the strong collider is described by an equilibrium distribution reduced by the factor $\Gamma(E_i) = \omega/(k(E_i) + \omega)$ assuming detailed balance. Sufficiently large polyatomic bath molecules, especially parent molecules, have been frequently considered⁷ as strong colliders with unit efficiency corresponding to $\langle \Delta E \rangle_{\text{down}} \ge 3500$ cm⁻¹ in thermal systems of average energy typically less than 10 kcal/mol. However, in the present system, $\langle \Delta E \rangle_{\text{down}}$ for the neat substrate was 1100 ± 100 cm⁻¹ in the temperature range of 660–706 K, and when the pressure-independent collision efficiency β is defined such that $\Gamma(E_i) = \beta \omega / (k(E_i) + \beta \omega), \beta$ for the parent molecule was found to be 0.32. Evidently, these results indicate that CH₂DCH₂Br is no longer a Lindemann strong collider at least in the temperature range of the present work.

The accurate determination $\langle \Delta E \rangle_{\rm down}$ for the parent molecule is of much importance in view of the error propagation in the evaluation of $(\Delta E)_{\text{down}}$ for the collision partner, especially in the case where energy-transfer parameters are deduced from differential dilution experiments at constant pressure of the parent gas. Since the bromoethane and chloroethane systems are similar in many aspects of molecular properties such as the dipole moment which is strongly correlated with intermolecular energy transfer,⁷ they are expected to behave in similar manner for the collisional activation/deactivation process. The value of $\beta = 0.19$ of chloroethane- d_0 , -1,1- d_2 , and - d_5 systems²⁹ may be used as a good guideline of the reliability of the present results for the substrate. Furthermore, the average energies $\langle \Delta E \rangle_{all}$ transferred in all upand down-transitions determined by the direct measurements⁵ indicate strong evidences that large polyatomic molecules and neat substrates are no longer strong colliders. These findings are also

further support to our findings.

Several studies⁷ on vibrational energy transfer have shown that there exists a strong correlation between $\langle \Delta E \rangle_{down}$, $\langle \Delta E \rangle_{all}$, or collision efficiency and a single molecular parameter of the bath gas. The boiling point $T_{\rm B}$ of collision partner interrelated with the intermolecular attractive force has shown the same trend with that of $\langle \Delta E \rangle_{\rm down}$. The present results were also in good accordance with the correlation, e.g., $\langle \Delta E \rangle_{\rm down} = 210$ cm⁻¹ and $T_{\rm B} = 4.5$ K for He, and $\langle \Delta E \rangle_{\rm down} = 675$ cm⁻¹ and $T_{\rm B} = 145.2$ K for CF₄ based on the EXP model.

 $\langle \Delta E \rangle_{\rm down}$ values for He and CF₄ deduced from the present work are somewhat smaller than those from other indirect thermal or external activation experiments,⁷ particularly from chemical activation studies on halogenated ethanes.¹⁸ The small $\langle \Delta E \rangle_{\rm down}$ value of about 1100 cm⁻¹ (SL model) for the substrate, consequently, has led to small $\langle \Delta E \rangle_{\rm down}$ values of 210 and 675 cm⁻¹ (EXP model) for He and CF₄, respectively. For the purpose of the direct comparison of {- $\langle \Delta E \rangle_{\rm all}$ } of the direct measurement^{5a} with $\langle \Delta E \rangle_{\rm down}$ of the present work, a relationship³⁰ for EXP model between two averages is used.

$$-\langle \Delta E \rangle_{\rm all} = \frac{\langle \Delta E \rangle_{\rm down}^2}{\langle \Delta E \rangle_{\rm all} + RT_{\rm e}}$$
(11)

where $T_e = T/[1 - 1(s' - 1)RT/E_0]$ and s' is the number of effective oscillators for real molecule. $\{-\langle \Delta E \rangle_{all}\}$ in eq 11 for He and CF₄ were found to be 50 and 337 cm⁻¹ at 706.4 K, respectively. These results are in better agreement with the direct measurements^{5a} from excited toluene and ethylcycloheptatriene systems, i.e., $\{-\langle \Delta E \rangle_{all}\} = 75-84$ cm⁻¹ for He, and 320-370 cm⁻¹ for CF₄, respectively.

Weak collision effects on the relative rate ratio can be well understood in terms of variations of the intermolecular energytransfer parameters of weak colliders. For a weak collider system with smaller average activation step size, more steps are required to reach the excited states compared with the strong collision system with a larger step size. Thus, for a given collision frequency, the steady-state populations of the reactant in the strong collision system are always larger than those in the weak collision system. Accordingly, due to the pressure dependency of $R(E_i)$ for a given ω , the relative rate ratios for weak collision are always larger than those for strong collision, although the former shows the smaller overall rate as well as the smaller rate of each reaction channel. These behaviors are in general agreement with our results by differential dilution experiments of weak colliders as displayed in Figure 2.

In the present study, two extreme forms of collisional transition probabilities, SL and EXP models, were used in order to fit the data on the neat substrate and collision partners He and CF₄. The experimental results were explained on either an EXP or a SL model basis, provided the average downward step size for each model was adjusted. The calculated results show that $\langle \Delta E \rangle_{\rm down}$ of an inefficient collision partner He for EXP model is smaller than that for SL model, while the trend is opposite when the average step size of the collider increases. The $\langle \Delta E \rangle_{\rm down}$ variation of the bath gas is in good agreement with the behavior predicted from the universal curves evaluated by Tardy and Rabinovitch.8 These curves denote the plots of collision efficiency vs. the reduced step-size parameter E' for SL and EXP models. The reduced step-size parameter, E', is defined by $\langle \Delta E \rangle_{\rm down} / \langle E^+ \rangle$, where $\langle E^+ \rangle$ is the Boltzman average energy of the reacting molecule in the second-order region.

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