Collisional Energy Transfer in the Two-Channel Thermal Decomposition of Bromoethane- $1, 1, 2, 2-d_4$

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The two-channel thermal decomposition of CHD_2CD_2Br (products $HBr + C_2D_4$, $DBr + CHDCD_2$), along with the decomposition of CH₃CH₂Br, has been studied by using the technique of very low-pressure pyrolysis (VLPP). Rate coefficients were obtained at pressures both so low that only gas/wall collisions occur (over the temperature range 950–1200 K) and dilute in various bath gases (pressures up to 10 Pa) over the range 1000–1070 K. Fitting these data by solution of the appropriate reaction-diffusion integrodifferential master equation yields the gas/wall collisional efficiency, the extrapolated high-pressure rate parameters, and the gas/gas collisional energy transfer probability function, P(E,E'). The extrapolated high-pressure rate coefficients are as follows: for CHD₂CD₂Br, $10^{13.20} \exp(-227.4 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ (HBr elimination), $10^{13.15} \exp(-230.2 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ (DBr elimination), and $10^{13.6} \exp(-221 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ for CH_3CH_2Br , in good agreement with those obtained by other methods. Gas/wall collision efficiencies (the wall being seasoned quartz) are ~0.6 at 1200 K, ~0.8 at 1000 K (with those for the d₄ species $\sim 10\%$ less than for the d₀), in accord with values estimated from the potential well depth. The data are moderately sensitive to P(E,E'). Assuming this for downward transitions to be a function of E -E' alone, we found that this function falls off more steeply than exponential, as found previously for chloroethane. Average bromoethane/M downward energy transfer values ($\langle \Delta E_{down} \rangle$) are 250 (M = Ne), 600 (M = CO₂), 850 $(M = C_2H_4)$, and 1200 (M = benzene) cm⁻¹, the variation of $\langle \Delta E_{down} \rangle$ with temperature being less than experimental uncertainty over the small experimental temperature range.

Introduction

An important task facing those studying unimolecular kinetics in the gas phase is the gathering of data on, and development and testing of theories for, collisional energy transfer between the reactant molecule (at high internal energies) and the bath gas. Apart from its intrinsic interest as a problem in molecular dynamics, the development of reliable predictive formulas for such collisional energy transfer is urgently needed for the correct interpretation of a growing body of uni- and termolecular rate data being obtained at high temperatures;¹ inter alia, the rate parameters are needed for modeling of complex combustion and aerochemical systems. It was first suggested by Chow and Wilson² that the pressure dependences of thermal rate coefficients for unimolecular decompositions which may occur via several channels should be sensitive to the assumed form of the collisional energy transfer probability function. This sensitivity becomes greater, the lower the pressure; however, complications due to wall effects also increase as the pressure is lowered. The present paper continues a series^{3,4} of studies of multiple-channel reactions utilizing a technique which deliberately uses wall effects, viz., the technique of very low-pressure pyrolysis (VLPP).^{5,6} Work on the two-channel decomposition of chloroethane-2- d^4 had shown that the sensitivity to assumed forms for the energy transfer probability function is particularly high when the two channels are separated by a difference in critical energy which is approximately the same as the average downward collisional energy transfer; this condition is readily met when the two channels differ by deuterium substitution. The present paper is on the two-channel decomposition of bromoethane- $1,1,2,2-d_4$:

$$CHD_2CD_2Br \rightarrow C_2D_4 + HBr \qquad (R_1)$$
 (1)

$$CHD_2CD_2Br \rightarrow CHDCD_2 + DBr$$
 (*R*₂) (2)

 R_1 and R_2 being the rate coefficients. The high-pressure relative rate coefficients (i.e., the isotope effect) have been obtained in a conventional flow system.⁷ A check on the consistency of the present data is the agreement of our extrapolated high-pressure rates with these values; a further check is furnished by high-pressure parameters from concomitant VLPP studies on (undeuterated) bromoethane, again to compare with those obtained directly by conventional experimental methods.^{8,9}

The main object of the present work is to provide further data on the collisional energy transfer of a highly internally excited reactant with a number of bath gases. The multiple-channel, pressure-dependent VLPP technique is sufficiently sensitive that it not only provides the average downward collisional energy transfer (as is also available from other methods¹⁰) but also gives information on the functional form of the probability distribution for this process. Our work on chloroethane-2-d showed unambiguously that, in this system, this probability distribution for downward transitions falls off more steeply than the exponential of the energy difference between initial and

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final states; it will be seen that this is also found in bromoethane-1,1,2,2- d_4 . In addition to reactant/bath gas energy transfer data, multiple-channel, pressure-dependent VLPP studies also yield the temperature-dependent gas/wall collisional energy transfer efficiency (the wall being seasoned quartz) and the RRKM parameters for the decomposition. The deliberate use of wall effects in VLPP does, of course, introduce additional parameters which must be fixed from the data, viz., those describing gas/wall collisional efficiency. However, this is compensated by (i) the fact that additional types of data are obtained (viz., rate coefficients for activation by gas/wall collisions alone), (ii) the particular experimental advantages of the system, which enable effects such as side reactions or wall-catalyzed processes to be readily detected should they occur,⁵ and (iii) the finding that the rate parameters obtained from the data fitting (including those for gas/wall collisional energy transfer) show good agreement with those from other methods. Thus, heterogeneous studies such as these provide a complement to homogeneous techniques and indeed provide access to a range of reactions and conditions which are not amenable to study by purely homogeneous methods. The gas/wall collision efficiency can be compared to those values obtained in similar systems by VLPP^{3,4} and by VEM,^{11,12} and with an empirical expression developed¹³ correlating this quantity with the boiling point (i.e., with the reactant/reactant potential well depth¹⁴).

Experimental Section

The VLPP experimental system and technique have been described in detail previously.³⁻⁵ The reactor has exit aperture diameters of 1.07, 3.36, and 10.1 mm, giving Knudsen cell collision numbers⁵ Z of 21 460, 2177, and 260, respectively. The gas/wall collision frequency ω_w is given by $(4.1 \times 10^3)(T/M)^{1/2}$ s⁻¹, where T is the temperature (K) and M is the molecular weight of reactant (amu).

Bromoethane- $1,1,2,2-d_4$ (Merck Sharp and Dohme of Canada, 98% D) and bromoethane- d_0 (May and Baker) were thoroughly degassed and vacuum distilled bulb to bulb. The bath gases for the pressure-dependence studies were neon (Matheson Research Grade, >99.995%), carbon dioxide (Matheson bone dry), ethylene (Matheson, C.P.), and benzene (BDH). Ethylene- $1,1,2-d_3$ (98% D) and ethylene- d_4 (99% D) for product identification and calibration were from Merck Sharp and Dohme of Canada.

The decomposition of CH_3CH_2Br was monitored by its major fragment mass spectral peak at m/e 29 using CO_2 at m/e 44 as an internal standard. The overall decay of CHD_2CD_2Br was monitored by the fragment peak at m/e33 while the individual pathways were monitored by C_2D_4 formation (HBr elimination) at m/e 32 and $CHDCD_2$ formation (DBr elimination) at m/e 31. Mass spectra were recorded for various calibration mixtures of $CHDCD_2$ with CHD_2CD_2Br , C_2D_4 with CHD_2CD_2Br , and $CHDCD_2$ with C_9D_4 .

Results and Discussion

It has been shown^{4,6} that, for multiple-channel, pressure-dependent VLPP experiments, the rate coefficient for the *i*th channel is given by

$$R_{i} = \int_{E_{0}}^{\infty} \mathrm{d}E \int_{V} \mathrm{d}\mathbf{r} \ G(E,\mathbf{r}) k_{i}(E) / \int_{0}^{\infty} \mathrm{d}E \int_{V} \mathrm{d}\mathbf{r} \ G(E,\mathbf{r}) \quad (3)$$

where E = internal energy, $k_i(E)$ = microscopic rate coefficient for channel *i*, **r** = position variable (the **r** integration being over the volume V of the vessel), and the eigenfunction $G(E,\mathbf{r})$ is given by the eigenvalue relation

$$-RG(E,\mathbf{r}) = D\nabla_{\mathbf{r}}^{2}G + \int dE' \left[P(E,E') \ G(E',\mathbf{r}) - P(E',E) \ G(E,\mathbf{r})\right] - k(E) \ G(E,\mathbf{r})$$
(4)

Here D = diffusion coefficient of reactant in bath gas, $k(E) = \sum_i k_i(E)$, and P(E,E') = normalized³ collisional energy transfer probability distribution function. The boundary conditions of eq 4 are

$$-D(\partial G/\partial r)|_{r=r_0} + \frac{1}{3}\beta_{\mathbf{w}}\omega_{\mathbf{w}}[Vf(E) - G(E,r_0)] = 0 \quad (5)$$

where r_0 = radius of vessel, f(E) = equilibrium population of reactant, and where the gas/wall collision efficiency is taken to have the functional form

$$\beta_{\rm w} = \min \left(1, a e^{-bT} \right) \tag{6}$$

where min refers to the minimum value. The $k_i(E)$ are parameterized by using RRKM theory, and the P(E,E') assumed to have a simple functional form such as

$$P(E,E') = \frac{1}{N(E')} \exp\left[\left(\frac{E-E'}{\alpha}\right)^n\right] \qquad E < E' \quad (7)$$

where N(E') is fixed by normalization and α is allowed to vary with temperature; P(E,E') for upward transitions (E > E') is determined by microscopic reversibility.

The pressure dependences of R_i at a given temperature are largely determined by the average downward energy transfer, $\langle \Delta E_{\text{down}} \rangle$:

$$\langle \Delta E_{\rm down} \rangle = \int_0^{E'} P(E,E')(E'-E) \, dE / \int_0^{E'} P(E,E') \, dE$$
(8)

For multiple-channel reactions where $\langle \Delta E_{\rm down} \rangle$ is of the order of the difference in critical energies, the VLPP pressure dependences of the R_i are, in addition, somewhat sensitive to the functional form in eq 7, as discussed below.

The various parameters in the above treatment are chosen to fit the entire data, some of which are shown in Figures 1-4. The mathematical procedures involved in convoluting k(E), P(E,E'), and β_w to obtain the pressure and temperature dependences of the R_i , by solution of eq 3-5, have been given elsewhere.^{4,6} The various parameters are found as follows.

The vibrational frequencies of CH_3CH_2Br were taken from spectroscopic data¹⁵ with the hindered internal rotation treated as a torsion; those for CHD_2CD_2Br were estimated by analogy with CH_3CH_2Br and other deuterated bromoethanes^{15,16} making use of isotopic frequency rules.¹⁷ First estimates of the frequencies and critical energies for the activated complexes were obtained by the usual means¹⁸ and then refined (along with the other parameters) to fit the data; although different sets of frequencies and E_0 may result in equally good data fits, the $k_i(E)$ curves so obtained are virtually identical over the energy range contributing significantly to the data. RRKM

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Figure 1. Temperature-dependent VLPP rate coefficients for the two decomposition channels of bromoethane-1,1,2,2-d4 at pressures so low that only gas/wall collisions occur; $R_1 = HBr$ formation, $R_2 = DBr$ formation. Points: experiment, for reactor collision numbers indicated. Lines: RRKM fit as described in text.



Bromoethane frequencies (cm⁻¹): (reactant) 3020, 2985, 2975, 2963,

- 2927, 562, 960, 1456, 1446, 1380, 1065, 1023, 1446,
- 1244, 780, 1185, 294, 243; (complex) 3055, 3045,
- 3060, 3040, 2200, 1395, 1385, 1400, 1380, 1300,
- 1005, 995, 1010, 990, 807, 479, 260 $E_0 = 218.5 \text{ kJ mol}^{-1}$, reaction path degeneracy = 3

Bromoethane-1, 1, 2, 2-d

- frequencies (cm⁻¹): (reactant) 2160, 2119, 2985, 2157, 2122, 520, 935, 1038, 1030, 1061, 824, 790, 1093, 940, 566, 838, 261, 180; (complex 1, HBr elimination) 2150, 2155, 2145, 2160, 2140, 1064, 1069, 1059, 1074, 1054, 940, 819, 809, 697, 566, 104, 515; (complex 2, DBr elimination) 2325, 2315, 2330, 2310, 1800, 1400, 1060, 1050, 1065, 1045, 940, 835, 825, 790, 663, 155, 415
- E_0 for HBr elimination = 225.8 kJ mol⁻¹, reaction path degeneracy = 1
- E_0 for DBr elimination = 230.4 kJ mol⁻¹, reaction path degeneracy = 2

collision diameters (nm): $CHD_2CD_Br/Ne, 0.42$ $CHD_{2}CD_{2}Br/CO_{2}, 0.475$ $CHD_{2}CD_{2}Br/C_{2}H_{4}, 0.49$ $CHD_{2}CD_{2}Br/C_{6}H_{6}, 0.54$

^a Reactants and activated complexes assigned the same moments of inertia product.

parameters are given in Table I, and the computed $k_i(E)$ in Figure 5, over the significant energy range. Values of a and b for β_{w} for CH₃CH₂Br were estimated from empirical expressions based on the normal boiling point,¹³ i.e., on the reactant/reactant potential well depth, as appropriate for reactant/seasoned quartz collisions; some small





Figure 2. Temperature-dependent VLPP rate coefficient for decomposition of bromoethane, at pressures so low that only gas/wall collisions occur. Points: experiment, for reactor collision numbers indicated. Line: RRKM fit as described in text.



Figure 3. Pressure-dependent VLPP rate coefficients for the two decomposition channels of CHD2CD2Br dilute (80:1) in bath gases Ne (1050 K) and CO2 (1045 K). Points: experiment. Lines: fit from solution of reaction/diffusion master equation. For CO2: exponential-cube P(E,E'), $\langle \Delta E_{down} \rangle = 600 \text{ cm}^{-1}$. For Ne: exponential-cube $(\langle \Delta E_{down} \rangle = 250 \text{ cm}^{-1})$ and exponential $(\langle \Delta E_{down} \rangle = 225 \text{ cm}^{-1})$.

adjustments to these estimates improve the fit. The values of a and b for CHD₂CD₂Br were taken to be such as to give $\beta_{\rm w}$ values ca. 10% lower than those for the undeuterated species (for temperatures in the range 1000–1200 K). This estimate of the difference in β_w between C_2H_5Br and C₂HD₄Br is based on the gas/wall average downward energy transfer values reported for cyclopropane and cyclo-



Figure 4. As in Figure 3, except for C_2H_4 and C_6H_6 bath gases, both at 1050 K; $\langle \Delta E_{down} \rangle = 850 (C_2H_4)$ and 1300 $(C_6H_6) \text{ cm}^{-1}$, exponential-cube P(E, E').



Figure 5. Computed RRKM microscopic reaction rates as function of energy for the two decomposition channels of CHD₂CD₂Br.

propane- d_{6} ¹² which give a decrease of ~15% in the β_{w} computed for the d_6 species as compared to the d_0 species, over the reported temperature range. This change in β_{w} on deuteration is, of course, not predicted by the simple empirical well-depth formula and presumably arises from more subtle effects such as the difference in density of states. However, the change in β_{w} involved is small, and within the expected error margin of the value estimated from the empirical well-depth formula. It should be noted, however, that variations in β_w of ca. 10% make a difference of $\sim 10\%$ in the average energy transfer values deduced from the data and moreover change the high-pressure Arrhenius parameters by less than the quoted uncertainties (see below). The final values of a and b were chosen to give, for C_2H_5Br , $\beta_w = 0.6$ at 1200 K, 0.85 at 1000 K (cf. the values of 0.5, 0.86 predicted from the empirical boiling point formulas) and, for CHD₂CD₂Br, $\beta_w = 0.55$ (1200 K), 0.77 (1000 K). Lastly, the values of α and n for P(E,E')in eq 7 were also varied to fit the data. Previous studies⁴ have shown that, despite an apparent plethora of adjustable parameters in this data fitting, the resulting values of $k_i(E)$ (as high-pressure parameters), P(E,E') (as values for α at each temperature and, to a lesser extent, the values for n), and β_{w} so obtained are reliable to within the quoted tolerances, provided that the fitting encompasses the sets

TABLE II: Bromoethane- $1, 1, 2, 2-d_4$ /Bath Gas Collisional Energy Transfer Results^{*a*}

bath gas		1000 K	1045 K	1050 K	1070 K	1100 K
Ne	$\langle \Delta E_{\rm down} \rangle$			250	275	300
	β			0.023	0.026	0.027
CO ²	$\langle \Delta E_{\rm down} \rangle$	500	600		700	
	β	0.086	0,10		0.12	
C_2H_4	$\langle \Delta E_{down} \rangle$			850	800	
	ß			0.17	0.15	
benzene	$\langle \Delta E_{down} \rangle$	1100		1300	1000	
	β	0.26		0.29	0.20	

^{*a*} (ΔE_{down}) values in cm⁻¹; computed with n = 3 in eq 7. $\beta = \text{collisional efficiency}$. Uncertainties in $\langle \Delta E_{\text{down}} \rangle$ and β are both ca. 10%.

of data obtained both without bath gas (gas/wall collisions only) and with bath gas (gas/wall and gas/gas collisions).

The high-pressure Arrhenius parameters computed from the $k_i(E)$ so obtained may be compared with those obtained directly in the high-pressure regime by other techniques. The high-pressure rate parameters calculated from the RRKM frequencies and critical energies obtained from the present VLPP experiments are subject to moderately large uncertainty because the reaction is well into the falloff regime under the accessible conditions: thus, for the present study, R/R_{∞} values (where R_{∞} is the high-pressure limiting rate coefficient) are ca. 10^{-2} at 1050 K. The high-pressure parameters are as follows: for C_2H_5Br , $R_{\infty}(s^{-1}) = 10^{13.6} \exp(-221 \text{ kJ mol}^{-1}/RT)$; for CHD_2CD_2Br , $R_{1,\infty}(s^{-1}) = 10^{13.20} \exp(-227.4 \text{ kJ mol}^{-1}/RT)$ (HBr elimination), $R_{2,\infty}(s^{-1}) = 10^{13.15} \exp(230.2 \text{ kJ mol}^{-1}/RT)$ RT) (DBr elimination); errors are estimated as $\pm 4 \text{ kJ mol}^{-1}$ for the activation energy and $\pm 10^{0.3}$ s⁻¹ for the frequency factor. These are in good agreement with high-pressure parameters obtained directly, viz., $R_{\infty}(C_2H_5Br) = 10^{13.4}$ $\exp(-224 \text{ kJ mol}^{-1}/RT)$,⁹ and for CHD_2CD_2Br ,⁷ $R_{1,\infty}/R_{2,\infty}$ = $10^{0.07} \exp(+3.9 \text{ kJ mol}^{-1}/RT)$ (compared with the present values of $10^{0.05} \exp(+2.8 \text{ kJ mol}^{-1}/RT)$ for this ratio). Absolute rate parameters for CHD₂CD₂Br have not been obtained hitherto.

The most significant results of our treatment are those for CHD₂CD₂Br/bath gas collisional energy transfer. Some of the fits to the pressure-dependent data are shown in Figures 3 and 4 (for all bath gases at 1050 K). For all bath gases and temperatures, the average downward energy transfer values, $\langle \Delta E_{\rm down} \rangle$, and concomitant gas/gas collision efficiencies, β , are given in Table II. In fitting the data, we made systematic variations both in $\langle \Delta E_{\text{down}} \rangle$ and in the functional form of P(E,E'), e.g., as in eq 7. Although moderately good fits could be obtained for a wide variety of functional forms, the best fits were for $n \ge 2$ in eq 7, at least for systems with small $\langle \Delta E_{\rm down} \rangle$ values (for the pressure and temperature range of the present data, there is virtually no difference in computed rate coefficients for large $\langle \Delta E_{\text{down}} \rangle$ for different values of *n*, provided that $\langle \Delta E_{\rm down} \rangle$ is kept fixed, although one would expect significant differences to occur over wider pressure ranges). This is illustrated by a comparison of exponential (n = 1)and exponential-cube (n = 3) fits in Figure 3, for Ne bath gas. The observation (at least for small $\langle \Delta E_{\rm down} \rangle$, when the distinction can be made) that P(E,E') for downward transitions falls off significantly faster than exponential was also made in studies on chloroethane-2-d.4 One notes that the fact that the introduction of an additional parameter (viz., n) into the data fitting leads to a significantly better fit in some cases (or, to be more specific, leads to an improved reduced χ^2 distribution) implies that the faster-than-exponential deduction is statistically meaningful.

The values of $\langle \Delta E_{\rm down} \rangle$ is given in Table II are in general agreement with those for similar collision partners in different systems.¹⁰ One notes that these values for deuterated bromoethane are much less than those for chloroethane:⁴ thus, at 1050 K, $\langle \Delta E_{\rm down} \rangle \simeq 550 \ {\rm cm}^{-1}$ for CH_2DCH_2Cl/Ne , $\simeq 250$ cm⁻¹ for CHD_2CD_2Br/Ne . While these collision systems alone are too limited to enable one to draw quantitative conclusions from such observations, these smaller $\langle \Delta E_{\rm down} \rangle$ values for the brominated molecule can be readily rationalized qualitatively by using a statistical argument as follows. This is based on premises similar to those used in some quantitative statistical models for energy transfer in such systems.¹⁹ One first notes that the bromoethane and chloroethane systems are similar in most respects except the densities of states. Thus, both molecules have almost identical dipole moments (both $\sim 6.8 \times 10^{-30}$ C m) indicating that the reactant/bath gas attractive forces are similar. In addition, the critical energies for the various decomposition channels are close (e.g., $\sim 220 \text{ kJ mol}^{-1}$ for C_2H_5Br , $\sim 230 \text{ kJ mol}^{-1}$ for C_2H_5Cl). On the other hand, the density of states for the bromo systems are much greater than those for the chloro; e.g., $\rho(E_0) \sim 4 \times 10^7$ per cm⁻¹ for CHD₂CD₂Br (E_0 for HBr elimination), $\rho(E_0) \sim 3 \times 10^6$ per cm⁻¹ for CH₂- DCH_2Cl (E_0 for HCl elimination). If all other factors are equal, one may legitimately suggest that collisional energy transfer will be governed by the density of states of the reactant/bath gas collision complex; for moderately small bath gases, this will be dominated by the density of states of the reactant. A crude statistical model for $\langle \Delta E_{\text{down}} \rangle$ is to assume that this is a decreasing function of the area of phase space accessible at a given energy E, since the ergodicity hypothesis invoked in this model implies that relatively less of the available phase space will be traversed during a collision (and thus less energy transferred) for larger $\rho(E)$, bearing in mind that the duration of a collision is essentially the same for both systems; one notes, of course, that the area of phase space $(\int \int d\mathbf{p} d\mathbf{q} \delta [E - \delta])$ $H(\mathbf{p},\mathbf{q})$), with the usual notation of classical mechanics) is $h\rho(E)$. Thus, under these circumstances it will be the reactant molecule with the lower density of states (i.e., the chloro systems) which will transfer more energy, in accordance with experiment.

The errors in the $\langle \Delta E_{\rm down} \rangle$ values in Table II are ~10%, as estimated directly by varying α and n in eq 7 over ranges which still fit the data acceptably. There appears to be a slight increase in $\langle \Delta E_{\rm down} \rangle$ with increasing temperature for Ne and CO₂ bath gases. This increase is however within experimental error, and the temperature range for the present studies is small. If this increase with temperature were to be a real effect rather than an artifact of experimental scatter, it would be opposite to the temperature dependence observed in energy transfer studies with other molecules over much wider temperature ranges.²⁰

It is important to note that there is no plateau observed in the pressure variation of the rate coefficients for CH- D_2CD_2Br in any of the VLPP experiments with bath gas

(e.g., Figures 3 and 4). A significant plateau was however observed for CH_2DCH_2Cl , for conditions where gas/gas collisions just began to compete with gas/wall collisions and where $\langle \Delta E_{\rm down} \rangle$ was particularly small.⁴ It was suggested that this effect was due to a small maximum at low energies in the $k_i(E)$ curves for CH₂DCH₂Cl, this maximum arising when the activated complex has no low-frequency $(\leq 400 \text{ cm}^{-1})$ vibrations, as predicted by (quantum) RRKM theory. It can be seen from Table I that the activated complexes for CHD₂CD₂Br have, by contrast, low-frequency (~150 cm⁻¹) modes, and thus the $k_i(E)$ have no maxima (see Figure 5). Therefore, in view of the similarity that otherwise holds between CH₂DCH₂Cl and CHD₂C- D_2Br in many respects, the nonobservation of a pressure plateau in VLPP/bath gas experiments on CHD₂CD₂Br is quite consistent with the suggested explanation for the plateau observed with CH₂DCH₂Cl.

Conclusions

The results of these multiple-channel, pressure-dependent VLPP experiments on CHD₂CD₂Br provide results which are useful in a number of aspects. The extrapolated high-pressure rate parameters for this molecule and for CH₃CH₂Br are in accord with those obtained directly by using different techniques, providing support for the complex mathematical modeling required in the data interpretation. The temperature-dependent gas/wall collisional energy transfer efficiencies, β_w , agree quite acceptably with those predicted by an empirical well-depth correlation formula, indicating that this formula can be used reliably to interpret, e.g., single-channel VLPP experiments (where the data alone are insufficient to simultaneously determine β_{w} and extrapolated high-pressure rate parameters). The most important results are those for CHD₂CD₂Br/bath gas collisional energy transfer, where the experimental data yield both the average downward energy transfer and information on the dependence of the energy transfer probability distribution function on the energy difference between initial and final states, this latter being much steeper than a simple exponential (for downward transitions). The actual values of $\langle \Delta E_{\text{down}} \rangle$ for the CHD₂CD₂Br system are considerably less than those in CH_2DCH_2Cl , a result which can be understood in terms of a simple statistical description. These results are thus useful additions to the small corpus of such energy transfer data which are sufficiently sensitive to furnish a proper test of theories for this process (other types of such data include information on the internal energy²¹ and temperature²⁰ dependences of $\langle \Delta E_{\text{down}} \rangle$), and thence to the development of tractable and accurate predictive models.

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Registry No. CHD_2CD_2Br , 25854-32-4; C_2H_5Br , 74-96-4; CH_2DCH_2Cl , 23072-56-2; Ne, 7440-01-9; CO_2 , 124-38-9; C_2H_4 , 74-85-1; C_6H_6 , 71-43-2.

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