

Intramolecular Isotope Effects in Terminal Unimolecular Reaction of $\text{CH}_2\text{DCH}_2\text{Br}^*$

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The principal objective of this study is to investigate the pressure and temperature dependence of the isotope effect in a competitive parallel processes between HBr and DBr elimination of $\text{CH}_2\text{DCH}_2\text{Br}$ in terms of the general characteristics of primary intramolecular isotope effect predicted by the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. This approach leads to two separate conclusions; first, the isotope effects on this competitive unimolecular reaction system are normal for all values of pressures of reactants. Second, the pressure dependence of the intramolecular isotope effect stems from the critical energy difference between two competing elimination processes and the variations of the steady-state populations of reactive energy levels with collision rates of reactants.

Study of competitive channel thermal unimolecular reaction in intermolecular energy transfer was suggested¹ some time ago. Recently, Rabinovitch, Jung and Klein² applied collisional competitive reaction spectroscopy to a two-channel processes of H and D atom atom migrations in the isomerization of cyclopropane-1,1,- d_2 at low-pressure. In this communication a preliminary investigation on the isotope effect in a two-channel parallel process thermal reaction of $\text{CH}_2\text{DCH}_2\text{Br}$ is reported. CH_2CH_2 and CH_2CHD produced by two-channel molecular elimination reaction were separated by 100 ft. AgNO_3 /Ethylene glycol column³ operated at 0 °C. Reaction products were analyzed by a two-stage gas chromatograph.⁴ The apparatus and experimental procedure were similar to that used by Park and Jung.⁵

The pressure dependences on the isotopic rate ratios, $k_{\text{H}}/k_{\text{D}}$, per β -hydrogen atom for thermal fractions of

TABLE 1: Pressure Dependences of Isotope Effects in Two-Channel Thermal Reaction of $\text{CH}_2\text{DCH}_2\text{Br}$ at 697.2 and 741.2 °K

At 697.2 °K		At 741.2 °K	
P, Torr	$k_{\text{H}}/k_{\text{D}}$	P, Torr	$k_{\text{H}}/k_{\text{D}}$
1.30	2.68	1.34	2.51
2.01	2.45	2.10	2.21
3.62	2.21	2.42	2.25
7.08	2.04	3.67	2.12
12.15	1.75	3.83	2.07
22.72	1.54	6.17	1.91
		12.88	1.64
		33.56	1.48

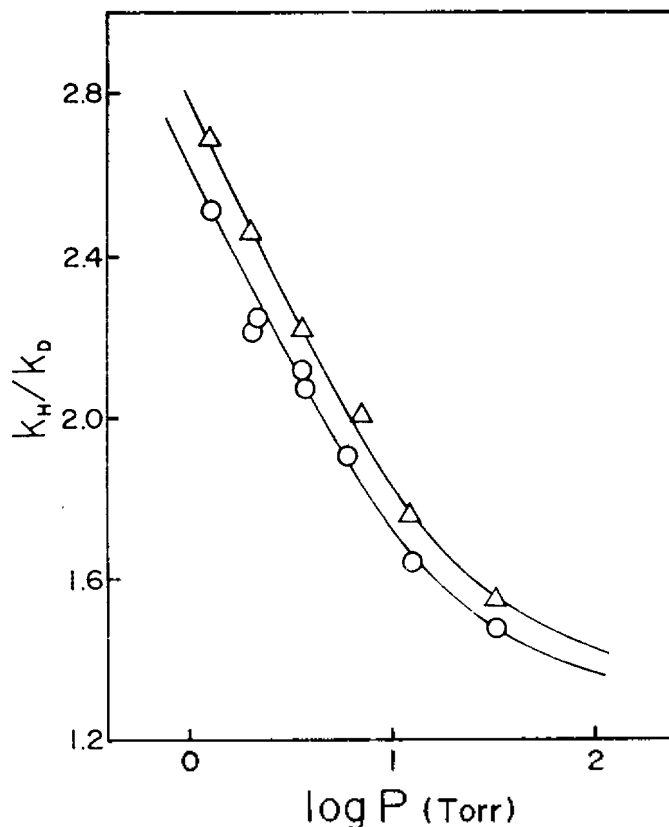


Figure 1. Pressure dependences of of isotope effects in competitive thermal reaction of $\text{CH}_2\text{DCH}_2\text{Br}$ at 697.2 (Δ) and 741.2 (o).

$\text{CH}_2\text{DCH}_2\text{Br}$ at 697.2 and 741.2 °K are given in Table 1 and plotted in Figure 1. At both temperatures the intramolecular isotope effects $k_{\text{H}}/k_{\text{D}}$, increases as pressures decrease. The activation energy difference, ΔE_a , and the ratio energy difference, E , and the ratio of Arrhenius pre-exponential factors between DBr and HBr elimination reactions at 3.60 mmHg were determined to be 829 ± 20 cal/mole and 0.20, respectively, from the temperature dependence of isotope effects given in Table 2 and plotted Figure 2.

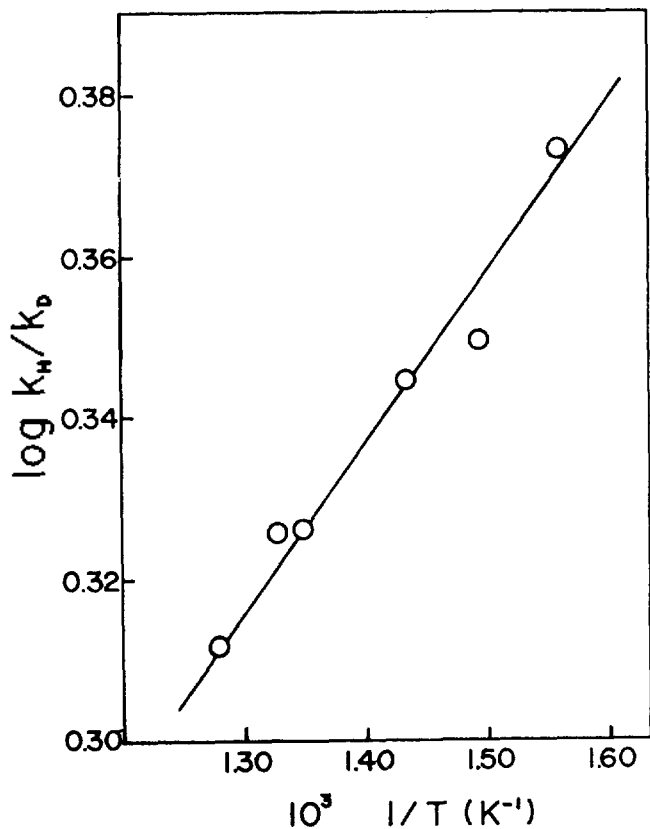
The quantum statistical RRKM description for the intramolecular isotope effect is given by

$$k_{\text{H}}/k_{\text{D}} = \frac{\int_0^{\infty} k_{\text{H}}(E_0^{\text{H}} + E_{\text{vr}}^{\ddagger}) P(E_0^{\text{H}} + E_{\text{vr}}^{\ddagger})_{ss} dE_{\text{vr}}^{\ddagger}}{\int_0^{\infty} k_{\text{D}}(E_0^{\text{D}} + E_{\text{vr}}^{\ddagger}) P(E_0^{\text{D}} + E_{\text{vr}}^{\ddagger})_{ss} dE_{\text{vr}}^{\ddagger}} \quad (1)$$

where $k(E_{\text{vr}}^{\ddagger})$ is the microscopic rate constant at a fixed energy level of activated complex and $P(E_{\text{vr}}^{\ddagger})_{ss}$ repre-

TABLE 2: Temperature Dependence of Isotope Effects in Competitive Decomposition Reaction of CH₂DCH₂Br at at 3.60 Torr

Temperature, ° K	k_D/k_H
641.2	2.37
668.9	2.23
697.2	2.21
741.2	2.12
753.1	2.11
781.2	2.05


Figure 2. Temperature dependence of isotope effects in two-channel thermal reaction of CH₂DCH₂Br.

sents the steady-state populations in reactive energy levels.

Isotope effect on the specific rate constants in the case for two activated complexes with the same non-fixed energy, E_{vr}^\ddagger , is expressed as

$$k_H(E_{vr}^\ddagger)/k_D(E_{vr}^\ddagger) = \frac{Z_H^\ddagger}{Z_D^\ddagger} \cdot \left(\frac{\sum P_H(E_{vr}^\ddagger)}{\sum P_D(E_{vr}^\ddagger)} \right) \times \left(\frac{N^*(E_{vr}^\ddagger + E_0^D)}{N^*(E_{vr}^\ddagger + E_0^H)} \right) \quad (2)$$

where Z^\ddagger is the partition functions for the adiabatic modes of activated complex; $\sum P(E_{vr}^\ddagger)$ is the sum of eigen states of the active degrees for activated complex; $N^*(E_{vr}^\ddagger)$ signifies the densities of states for the molecule. The first term of Eq. 2 represents a centrifugal effect. Changes in the moments of inertia for the overall rotations are likely to be small and partially compensating. The second term signifies the statistical-weight contribution. In deuterium substitution of the activated complex, HBr elimination lowers the vibrational frequencies more significantly than in DBr splitting

of the complex, and hence the energy level spacing becomes denser. Therefore, $\sum P_H(E_{vr}^\ddagger)$ is always larger than $\sum P_D(E_{vr}^\ddagger)$. The third term is due to the critical energy difference between two competitive parallel processes. Since the densities of molecular quantum states are increasing functions of the reactive energy levels, the values of the term are always larger than unity. Therefore, the isotope effect on the microscopic rate constants become normal over all values of E_{vr}^\ddagger . Since $E_0^H < E_0^D$ and $P(E_0^H + E_{vr}^\ddagger) > P(E_0^D + E_{vr}^\ddagger)$, the intramolecular isotope effects in two-channel thermal reaction of CH₂DCH₂Br are normal over the whole pressure range.

In unimolecular thermal reaction, the ratio of steady state population to equilibrium population (fractional depletion) decreases as the collision rate decreases but increases with a decrease in E_{vr}^\ddagger .

For the competitive channel reaction of CH₂DCH₂Br, the steady-state distribution function corresponding to DBr elimination reaction is displaced to higher energy level due to the higher critical energy required for the reaction than the HBr elimination reaction. Therefore, the steady-state population decreases more rapidly at higher energy levels. At low pressures, the over-all rate constant k_D for DBr elimination decreases faster than k_H for HBr elimination, so that the isotope effect increases with a decrease of pressure. It is also noted that, although the isotope effect increases with decreasing pressure, the over-all and individual rate constants decrease with decreasing pressure. It is interesting to note that Seter and Siefert⁷ found a similar trend for k_H/k_D in a chemical activation system, while Rabinovitch *et al.*⁸ reported a decrease in isotope effect as pressure decreased for an intermolecular reaction although k_H/k_D was greater than 1.

Theoretical calculations based on RKKM theory qualitatively support the experimental observations. This preliminary study indicates a need to extend experimental study for higher pressures, including temperature profiles.

References

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