

## Non-Bonded Interaction Effects on Cis-Trans Isomerization of 1-Bromopropene

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The hindered internal rotation effect of methyl group on chemical reaction was studied for *cis-trans* isomerization reaction of 1-bromopropene system using RRKM technique. A comparative study of the isomerization rates was also performed between the rigid and allowed internal rotations. The calculated rate of rigid *cis-trans* isomerization of 1-bromopropene was shown to be three times higher than its other halogenated propene homologues with its internal rotations and found to be in good agreement with experimental observations. These findings could be explained reasonably well in terms of the differences of the rotational barrier heights among halogenated propenes and correlated with the relatively low internal rotation barrier of *cis*-1-bromopropene, 230 cal/mol, compared to those of other *cis*-1-halopropenes, 700-800 cal/mol, and *trans*-1-halopropenes, 2.0-2.4 kcal/mol.

### Introduction

The thermodynamic and kinetic effects by the methyl hindered internal rotation barrier heights of *cis* and *trans*-1-halopropenes have shown considerable interests in elucidating more reliable and significant information on molecular geometrical configuration and non-bonded interaction between hydrogen and halogen atom of 1-halopropenes.

A number of rotational spectroscopic studies for 1-halopropenes and related systems<sup>1-3</sup> have revealed that *cis*-isomers have lower potential barrier hindering the rotation of methyl group about the C-C single bond than *trans*-isomers. The barrier heights,  $V_3$  of *trans*-CH<sub>3</sub>CH=CHX and *trans*-CH<sub>3</sub>CH=CHCH<sub>3</sub> vary from 2.0 to 2.4 kcal/mol, while those of *cis*-isomers do not exceed 1.0 kcal/mol. The lowering of the barrier from *trans* to *cis* has been well explained<sup>4</sup> by an assumption that the interaction between halogen and methyl hydrogens is governed by a Morse-like potential with a steep repulsive state at short separations of H and X, and a gentle attractive slope at larger separations. These lowering phenomena of barrier heights of *cis*-1-halopropenes tend to be more prominent for larger halogen atom substituted in 1-halopropene compounds as listed in Table 1. This tendency further supports the existence of nonbonded interaction<sup>2</sup> between halogen and methyl hydrogens by the reason that the van der Waals radii overlap is greater in *cis*-CH<sub>3</sub>CH=CHBr than in *cis*-CH<sub>3</sub>CH=CHCl and *cis*-CH<sub>3</sub>CH=CHF. The double bond length in 1-bromopropene is shorter than in its fluorine and chlorine homologues while van der Waals radius of Br is opposite in its order from those of F and Cl.

In spite of the increasing interest, the isomerization reaction system of 1-halopropenes has been relatively unknown<sup>5</sup> compared to an extensive studies on other similar systems, *i.e.*, CH<sub>3</sub>CH=CHCN<sup>6</sup>, CH<sub>3</sub>CH=CHCH<sub>3</sub><sup>7-9</sup>, CHCl=CHCl<sup>10</sup> and CHD=CHD<sup>11</sup>.

In this paper we report the study of the nonbonded interaction effects of *cis-trans* isomerization reaction of 1-halopropenes utilizing the isomerization reaction of 1-bromopropene

**Table 1.** Barrier Heights ( $V_3$ , cal/mol) of Methyl Group in *Cis*- and *Trans*-1-halopropenes and Related Compounds

Compounds	$V_3$ ( <i>cis</i> )	$V_3$ ( <i>trans</i> )	Reference
CH <sub>3</sub> CH=CHF	1060	2220	1
CH <sub>3</sub> CH=CHCl	602	2170	1
CH <sub>3</sub> CH=CHBr	230	2120	16
CH <sub>3</sub> CH=CHCH <sub>3</sub>	750	1950	25
CH <sub>3</sub> CH=CHCN	1400		1
CH <sub>3</sub> CH=CH <sub>2</sub>		1978 <sup>a</sup>	1
CH <sub>3</sub> -CH <sub>3</sub>		2900 <sup>a</sup>	14

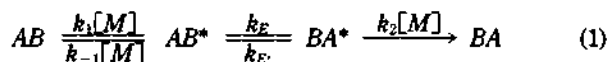
<sup>a</sup>No isomers are available

as a model of prototype reaction. The effect of the molecular geometrical configuration to the *cis-trans* isomerization reaction of 1-halopropenes was evaluated from the internal rotation effects to the reaction rates.

### Calculations

#### Formulation

**Cis-trans Isomerization Reaction.** *Cis-trans* isomerization reaction differs from ordinary decomposition in that the newly-formed product molecules may contain a large amount of vibrational energy as suggested by Lin *et al.*<sup>12</sup>. In a decomposition reaction the excess energy may be partitioned among reaction fragment molecules as internal and some as relative translational energies. Before deactivation the energy-rich molecule may easily go back to a reactant molecule. The reverse reaction depends strongly on the heat of reaction. The reaction scheme for an isomerization can be written by,



where  $M$  is a collision partner.  $AB^*$  and  $BA^*$  are the energized molecules, each capable of changing into its isomer without acquiring further energy.

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By steady-state treatment and integrating over all possible energy states above threshold value  $E_0$ , the forward rate expression becomes,

$$k_{for} = \int_{E_0}^{\infty} k_E K_E dE / (1 + (k_E + k_E^-) / Zp) \quad (2)$$

where  $k_{for}$  is the overall forward rate constant for isomerization process and  $K_E dE = d(k/k_{-1})$  = the fraction of energized molecules having energy between  $E$  and  $E + dE$ .  $Zp = k_{-1}[M] = k_2[M]$ .  $Z$  is the collision frequency.

The microscopic rate coefficients of forward reaction  $k_E$  and reverse reaction  $k_E^-$ , and the equilibrium fraction  $K_E$  can be calculated. In this study we have calculated these values utilizing a statistical quantum mechanical model, RRKM, and the procedure developed in author's lab and given by,

$$k_E = (L^+ / h) (Q_1^+ / Q_1) (\Sigma P(E_{v^+}) / N(E^+ + E_0)) \quad (3)$$

$$k_E^- = (L^- / h) (Q_1^- / Q_1) (\Sigma P(E_{v^-}) / N'(E^+ + E_0 - \Delta H_0^0)) \quad (4)$$

$$K_E = N(E^+ + E_0) \exp(-E/RT) / Q \quad (5)$$

where  $N(E^+ + E_0)$ ,  $N'(E^+ + E_0 - \Delta H_0^0)$  and  $\Sigma P(E_{v^+})$  are the densities of energy states of *cis*-isomer, *trans*-isomers and the sums of states of activated complex, respectively.  $L^+$  and  $L^-$  represent the reaction path degeneracies of forward and reverse reactions.  $\Delta H_0^0$  and  $E_0$  are the heat of reaction at 0 K and the critical energy for forward reaction.  $Q_1$ ,  $Q_1^+$ ,  $Q$  and  $h$  are the rotational partition functions of molecule and activated complex, the ro-vibrational partition function of molecule and the Planck constant, respectively. In high pressure limit, Eq. (2) reduces to a well known form of rate expression by the conventional RRKM formulation and activated complex theory.

**Hindered Internal Rotation.** If two local groups in a molecule are loosely bound (<3 kcal/mol) and rotate about their binding axis relatively freely, this restricted relative motion can be described by an internal rotation and the corresponding moment or reduced moment of inertia,  $I_r$ , in terms of local moments,  $I_1$  and  $I_2$ ,

$$I_r = I_1 I_2 / (I_1 + I_2). \quad (6)$$

The wave equation for the relative motion of the two tops is then,

$$-(\hbar^2 / 2I_r) (d^2 \phi / d\phi^2) + [U(\phi) - E] \phi(\phi) = 0 \quad (7)$$

where  $U(\phi) (= V_3(1 - \cos 3\phi))$  for methyl group rotation<sup>14</sup> is the potential and  $\phi$ , the angle of rotation. The period of the periodic potential function is given by  $2\pi/n$ , where a constant  $n$  is related to the symmetry of rotating group, e.g.,  $n=3$  for methyl group. The  $V_3$  is the rotational barrier height. Various degrees of approximation techniques<sup>13,14</sup> are available between harmonic-oscillator and free-rotor for solution of Eq. (7). In brief, four prototypes of these are: 1) *Harmonic-Oscillator Approximation*. For high barrier, the potential function  $U(\phi)$  is approximated by  $U(\phi) = 9V_3\phi^2/4$  and the wave equation represents a simple harmonic oscillator. The energy levels are, thus, given by  $E_n = (n + 1/2)h\nu$   $n=0, 1, 2, \dots$  and  $\nu = (3/2\pi)(V_3/I_r)^{1/2}$ ; 2) *Free-Rotor Approximation*. When the energy level of interests is much higher than the barrier heights, the wave equation can be solved by treating the inter-

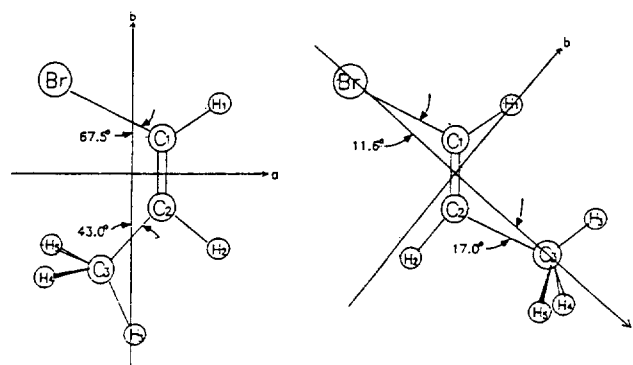


Figure 1. Molecular structural conformations and principal moment of inertias of *cis*- and *trans*-1-bromopropene.

nal rotation as a free-rotor. The energy levels are, then,  $E_n = n^2 \hbar^2 / 8\pi^2 I_r$ ,  $n=0, \pm 1, \pm 2, \dots$ ; 3) *Pitzer-Rotor Approximation*. A modified free rotor approximation method is also known as a Pitzer rotor method where potential function  $U(\phi)$  in Eq. (7) has been replaced by its average value,  $V_3/2$ . The energy levels in this method are,  $E_n = n^2 \hbar^2 / 8\pi^2 I_r + V_3/2$   $n=0, \pm 1, \pm 2, \dots$ ; 4) *True Hindered Rotor*. In order to obtain the true hindered rotor energy levels, the wave Eq. (7) must be solved accurately. By high energy approximation of second order perturbation method with free rotor basis, i.e.,  $H = H_0 + H_1$ ,  $H_0 = -(\hbar^2 / 8\pi^2 I_r) d^2 / d\phi^2$  and  $H_1 = V_3(1 - \cos 3\phi) / 2$ , the Schrodinger equation,  $H\psi(\phi) = E\psi(\phi)$ , then, gives the true hindered energy levels,  $E_n = m^2 \hbar^2 / 2I_r + V_3/2 + V_3^2 I_r / 4 \hbar^2 (m^2 - 9)$   $m=0, \pm 1, \pm 2, \dots$ .

### Computation

The microscopic rate constants of *cis-trans* isomerization reaction of 1-bromopropene were calculated using vibrational frequencies assigned by Elst *et al.*<sup>15</sup> and supplemented with the internal rotation barrier values compiled by Good *et al.*<sup>16</sup>. The structural data of *trans*-1-bromopropene were taken from the reported values<sup>2</sup> and those of *cis*-1-bromopropene were deduced from *trans* structure utilizing the differences between *trans*-1-bromopropene and *cis*-1-chloropropene. The principal and reduced moments of inertia of *cis*- and *trans*-1-bromopropene obtained<sup>17</sup> were well agreed with the values of Lielmezs<sup>18</sup> within 9.8%. In eclipsed conformation, on hydrogen of methyl group and ethylenic bromine were assumed to be on the same plane for calculation of principal and reduced moments of inertia between eclipsed and staggered molecules were of negligibly small difference. The eclipsed conformations of *cis*- and *trans*-1-bromopropene are shown in Figure 1 and structural parameters are summarized in Table 2. The vibrational frequencies and calculated moments of inertia used in this work for *cis*- and *trans*-molecules are listed in Table 3.

A twisted singlet state was adopted for an activated complex from a satisfactorily proven system in the studies of various thermal *cis-trans* isomerization reactions of substituted ethylenes<sup>19</sup>. For vibrational frequency assignment, the C-C stretching and the closely related frequencies were adjusted to fit the experimental Arrhenius parameter<sup>20</sup> and the rest of frequencies were assigned the same as those of the reactant molecules. The internal rotation barrier height of activated complex was assumed a nearly twisted single

**Table 2.** Structural Parameters, Bond Lengths and Bond Angles of *Cis-* and *Trans*-1-Bromopropene.

<i>cis</i> -1-bromopropene	<i>trans</i> -1-bromopropene
Bond length (cm×10 <sup>8</sup> )	
$r(C_1=C_2)=1.336^a$	$r(C_1=C_2)=1.336^a$
$r(C_2-C_3)=1.501$	$r(C_2-C_3)=1.501$
$r(C_1-H)=1.091$	$r(C_1-H)=1.091$
$r(C_2-H)=1.090$	$r(C_2-H)=1.090$
$r(C_3-H)=1.090$	$r(C_3-H)=1.090$
$r(C_1-Br)=1.884$	$r(C_1-Br)=1.884$
Bond Angle (°)	
$\angle(C_2=C_1-H)=120.5^b$	$\angle(C_2=C_1-H)=120.5^b$
$\angle(C_3-C_2-C_1)=124.3$	$\angle(C_3-C_2-C_1)=124.3$
$\angle(C_1=C_2-H)=119.0$	$\angle(C_1=C_2-H)=119.0$
$\angle(C_3-C_2-H)=116.7$	$\angle(C_3-C_2-H)=116.7$
$\angle(H-C_3-H)=107.7$	$\angle(H-C_3-H)=107.7$
$\angle(C_2=C_2-Br)=126.4$	$\angle(C_2=C_1-Br)=122.1$

<sup>a</sup>Bond lengths of *cis* and *trans* isomers are all taken from ref. 2 assuming bond length difference between *cis* and *trans* structure of 1-halopropene is much small as shown in refs. 1 and 2. <sup>b</sup>Bond angles of *cis* and *trans* isomers were also taken from ref. 2, and the  $\angle(C_2=C_1-Br)$  of *cis* isomer was determined by our own accord referring to the *trans*-1-chloropropene as shown in ref. 1.

**Table 3.** Vibrational Frequencies, Principal and Reduced Moments of Inertia of *Cis-* and *Trans*-1-Bromopropenes

<i>cis</i> -1-bromopropene	<i>trans</i> -1-bromopropene
Fundamental frequencies (cm <sup>-1</sup> ) <sup>a</sup>	
3102, 3034, 2978	3078, 3029, 2980
2960, 2947, 1638	2961, 2937, 1637
1456, 1444, 1388	1461, 1446, 1387
1312, 1212, 1070	1292, 1225, 1087
1041, 936, 925	1041, 952, 931
765, 684, 677	743, 729, 677
494, 382, (194) <sup>b</sup>	355, 250, (210) <sup>b</sup>
Principal moments of inertia (g·cm <sup>2</sup> ×10 <sup>39</sup> )	
$I_A=6.238$	$I_A=2.087$
$I_B=34.454$	$I_B=49.762$
$I_C=40.173$	$I_C=51.331$
Reduced moment of inertia (g·cm <sup>2</sup> ×10 <sup>39</sup> )	
$I_{red}=0.519$	$I_{red}=0.404$
Internal rotation barrier height (cal·mol <sup>-1</sup> )	
230	2120
Internal rotation constant (cm <sup>-1</sup> )	
5.393	6.932
Molecular weight <sup>d</sup> (g/mol)	
120.0	120.99

<sup>a</sup>Frequencies obtained from ref. 15. <sup>b</sup>Torsional frequency was used reaction coordinate. <sup>c</sup>Calculated values in this work using the structural parameters given in Table 2. <sup>d</sup>Molecular weight difference due to the isotopic ratio. These values were taken from ref. 18.

**Table 4.** Adjusted Vibrational Frequencies and Structural Parameters of Activated Complex

Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	Bond length (cm×10 <sup>8</sup> ) <sup>b</sup>	Bond angle (°) <sup>c</sup>
3000, 3000, 3000	$r(C_1-C_2)=1.48$	$\angle(C_2-C_1-H_1)=120.5$
3000, 2800, 2590	$r(C_2-C_3)=1.52$	$\angle(C_3-C_2-H_2)=118.7$
2759, 2349, 1230	$r(C_1-H_1)=1.10$	$\angle(C_1-C_2-C_3)=121.3$
1230, 2340, 1200	$r(C_2-H_2)=1.10$	$\angle(C_1-C_2-H_2)=120.0$
780, 450, 230	$r(C_3-H)=1.10$	$\angle(H-C-H)=108.7$
340, 234, 456	$r(C_1-Br)=1.92$	$\angle(C_2-C_1-Br)=123.1$
123, 123		
Principal moments of inertia (g·cm <sup>2</sup> ×10 <sup>39</sup> )		Reduced moment of inertia (g·cm <sup>2</sup> ×10 <sup>39</sup> )
$I_A=4.934$		$I_{red}=0.510$
$I_B=45.219$		
$I_C=47.507$		
Internal rotation barrier height (V <sub>3</sub> , cal/mol) <sup>d</sup>		
2920		
Internal rotation constant (cm <sup>-1</sup> )		
5.494		
Critical energy of forward reaction (E <sub>0</sub> , cm <sup>-1</sup> )		
19530		
Enthalpy difference between <i>cis</i> and <i>trans</i> isomer at 0 K (ΔH <sub>0</sub> <sup>o</sup> , cal·mol <sup>-1</sup> ) <sup>e</sup>		
123.286		

<sup>a</sup>Adjusted frequencies to the experimental A-factor of ref. 20.

<sup>b</sup>Bond length and bond angle of activated complex were assigned similar manner to those of *cis* and *trans* isomers assuming a twisted singlet state for an activated complex. <sup>c</sup>Moment of inertia calculated using the structural data given above. <sup>d</sup>Assumed barrier height referring to similar compounds. <sup>e</sup>Calculated internal rotation constant. <sup>f</sup>Taken from ref. 20. <sup>g</sup>Calculated using the equilibrium constant of ref. 21 and thermodynamic values of ref. 18.

bond by the comparison with those of similar systems, *i.e.*, CH<sub>3</sub>CH=CHBr, CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub><sup>25</sup> and CH<sub>3</sub>CH<sub>2</sub>Br<sup>25</sup>. The vibrational frequencies and structural parameters of activated complex, and other related data used in this work are summarized in Table 4.

ΔH<sub>0</sub><sup>o</sup> was calculated using the thermodynamic functions of *cis*- and *trans*-1-bromopropene<sup>18</sup> an experimental equilibrium constant,<sup>21</sup> *cis/trans*≈4.02 at room temperature. The reaction path degeneracies L<sup>+</sup> and L<sup>+</sup> are all 2 since the isomerization can occur by twisting about the double bond in either direction. The torsional mode of the double bond was considered as the reaction coordinate in the same manner as other similar substituted ethylenic systems.

The sums, ΣP(E<sub>v</sub><sup>+</sup>), and the densities, N(E<sup>+</sup>+E<sub>0</sub>), N'(E<sup>+</sup>+E<sub>0</sub>-ΔH<sub>0</sub><sup>o</sup>) of eigen states were evaluated by direct counting method using Beyer-Swinehart algorithm<sup>22</sup> extended by Stein *et al.*<sup>23</sup> The collision number Z used in this study was obtained from the simple collision theory. The collision diameter σ<sub>d</sub> was determined by the correlation method by Stiel and Thodes<sup>24</sup>, *i.e.*, σ<sub>d</sub>=0.785 V<sub>c</sub><sup>1/3</sup>, where V<sub>c</sub> is the critical molar volume in cm<sup>3</sup>/mol. The calculated collision diameters of *cis*- and *trans*-1-bromopropene were 6.56 and 6.74 Å respectively.

**Table 5.** Rate Constants of *Cis-Trans* Isomerization of 1-Bromopropene with Rigid and Allowed Internation Rotations at 650.2 and 750.2 K

P (torr)	T (K)	$k_{rig}$ ( $s^{-1}$ ) <sup>a</sup>	rate constant ratio <sup>b</sup>			
			$R_I$	$R_{II}$	$R_{III}$	$R_{IV}$
0.01	650.2	$7.44 \times 10^{-7}$	0.93	2.52	2.32	2.58
	750.2	$1.70 \times 10^{-4}$	0.92	2.14	2.05	2.43
0.10	650.2	$1.29 \times 10^{-6}$	0.98	2.71	2.63	3.28
	750.2	$3.55 \times 10^{-4}$	0.96	2.31	2.31	3.14
1.00	650.2	$1.61 \times 10^{-6}$	1.00	2.83	2.80	3.28
	750.2	$5.12 \times 10^{-4}$	0.99	2.43	2.50	3.76
100.0	650.2	$1.72 \times 10^{-6}$	1.01	2.88	2.87	3.90
	750.2	$5.90 \times 10^{-4}$	1.01	2.50	2.60	4.12
$\infty$	650.2	$2.16 \times 10^{-6}$	1.01	2.86	2.86	3.91
	750.2	$7.20 \times 10^{-4}$	1.01	2.49	2.60	4.11

<sup>a</sup> $k_{rig}$  are the rate constants with rigid internal internal rotations of 1-bromopropene for all of *cis*- and *trans*-molecules and activated complex. <sup>b</sup> $R_I$ ,  $R_{II}$ ,  $R_{III}$ , and  $R_{IV}$  represent the ratios of the rate constant of rigid to allowed internal rotation systems, i.e., rigid to free rotor, to Pitzer rotor, to true hindered rotor, and to harmonic oscillator approximation, respectively. In allowed systems, the given approximation method was applied same manner to *cis*- and *trans*-molecules and activated complex of 1-bromopropene in all cases.

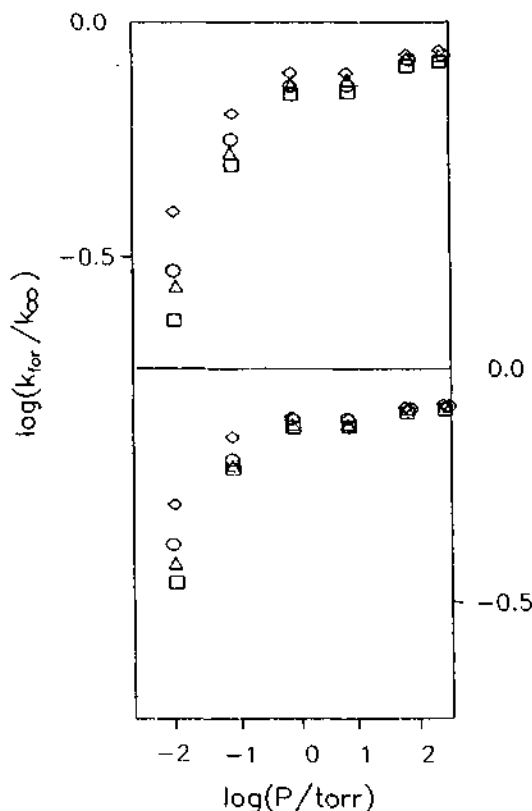
## Results and Discussions

**Results.** *Cis-trans* isomerization reaction rate coefficients of 1-bromopropene have been calculate adopting RRKM formalism the rigid and hindered internal rotation. Comparative studies were also made among four known approximation techniques of hindered rotor treatments.

Calculated rate coefficients and the ratio of the rigid to various degrees of allowed internal rotations are listed in Table 5 at 650.2 and 750.2 K, and at pressure ranges from 0.01 torr to high-pressure limit, and displayed in Figure 2. In the table, the rate coefficient and the ratio to various internal rotors are dependent strongly on the rotor models showing decreasing tendencies with the degrees of looseness of the rotor while the trends are opposite with pressure and temperature increase. The ratio varies from *ca.* 1.0 with free rotor to *ca.* 4.0 at harmonic oscillator approximation and *ca.* 3 at the true hindered rotor. In order to obtain the configuration information of *cis*-1-bromopropene, the calculations were repeated assuming that the *cis* molecule was the free rotor and harmonic oscillators, respectively, and the activated complex and *trans* molecule were true hindered rotors, and the results are listed in Table 6.

The effects of barrier heights were studied by varying that of *cis* molecule from 101 cal/mol corresponding to a half of the barrier height, to 602 cal/mol corresponding to that of *cis*-1-chloropropene, to 2120 cal/mol of *trans*-1-bromopropene, and to 2920 cal/mol of activated of activated complex of 1-bromopropene with fixed barriers of *trans* molecule and activated complex. As shown in Table 7, the rate constant ratios of the rigid to the internal rotation allowed systems have decreased by an increase of the barrier of *cis* molecule.

**Discussion.** The hindered internal rotation effects on

**Figure 2.** Pressure dependences of calculated *cis-trans* isomerization rates of *cis*-1-bromopropene at 650.2 K (right) and 750.2 K (left) with rigid and allowed internal rotation systems of methyl group.  $\square$ : rigid system;  $\circ$ : true hindered systems;  $\triangle$ : free rotor approximation;  $\diamond$ : harmonic oscillator approximation.**Table 6.** Isomerization Rate Constants with The Free Rotor and Harmonic Oscillator Assumed *Cis*-Molecule at 750.2 K

Pressure (torr)	$k_{rig}$ <sup>a</sup>	$k_{rig}/k_{cis-1}$ <sup>b</sup>	$k_{rig}/k_{cis-2}$ <sup>c</sup>
0.01	$1.70 \times 10^{-4}$	2.13	0.85 (2.05) <sup>d</sup>
0.10	$3.55 \times 10^{-4}$	2.40	0.92 (2.05)
1.0	$5.12 \times 10^{-4}$	2.60	0.97 (2.05)
100.0	$5.90 \times 10^{-4}$	2.71	0.99 (2.60)
$\infty$	$7.20 \times 10^{-4}$	2.71	0.99 (2.60)

<sup>a</sup> $k_{rig}$  are the rate constants with rigid internal internal rotations of 1-bromopropene for all of *cis*- and *trans*-molecules and activated complex. <sup>b</sup> $k_{cis-1}$ , *cis*-molecule with free rotor only and *trans*-molecule and activated complex with true hindered rotors. <sup>c</sup> $k_{cis-2}$ , *cis* molecule with harmonic oscillator and *trans*-molecule and activated complex with true hindered rotors. <sup>d</sup>The values in parenthesis are given to compare with the  $R_{IV}$  of table 5.

*cis-trans* isomerization reaction of 1-halopropene listed in Table 5 show very similar results with those from the observed values of other substituted ethylene systems.<sup>19</sup> Fall-off behaviors shown in Figure 2 are also close to the isomerization of 2-butene systems<sup>12</sup>, e.g., the difference of  $\log(k_{iso}/k_{\infty})$  over the pressure range from 0.01 to 100 torr at 742 K is *ca.* 0.4 for 2-butene, and *ca.* 0.5 for 1-bromopropene system in this work over the same pressure region and at 750.2 K. The detailed evalua-

**Table 7.** Isomerization Rate Constants at Variation of Barrier Heights of *Cis*-1-Bromopropene at 750.2 K

Barrier heights (cal/mol) <sup>a</sup>	pressure (torr)	$k_{rg}^b$ (s <sup>-1</sup> )	$k_{hin}^c$ (s <sup>-1</sup> )	$k_{rg}/k_{hin}$
115	0.01	$1.70 \times 10^{-4}$	$8.10 \times 10^{-5}$	2.10
	1.00	$5.12 \times 10^{-4}$	$1.99 \times 10^{-4}$	2.57
	∞	$7.20 \times 10^{-4}$	$2.69 \times 10^{-4}$	2.68
230	0.01	$1.70 \times 10^{-4}$	$8.31 \times 10^{-5}$	2.05
	1.00	$5.12 \times 10^{-4}$	$2.05 \times 10^{-4}$	2.50
	∞	$7.20 \times 10^{-4}$	$2.77 \times 10^{-4}$	2.60
602	0.01	$1.70 \times 10^{-4}$	$9.19 \times 10^{-5}$	1.85
	1.00	$5.12 \times 10^{-4}$	$2.27 \times 10^{-4}$	2.26
	∞	$7.20 \times 10^{-4}$	$3.07 \times 10^{-4}$	2.34
2120	0.01	$1.70 \times 10^{-4}$	$1.57 \times 10^{-4}$	1.08
	1.00	$5.12 \times 10^{-4}$	$4.00 \times 10^{-4}$	1.28
	∞	$7.20 \times 10^{-4}$	$5.44 \times 10^{-4}$	1.32
2920	0.01	$1.70 \times 10^{-4}$	$2.02 \times 10^{-4}$	0.84
	1.00	$5.12 \times 10^{-4}$	$5.22 \times 10^{-4}$	0.98
	∞	$7.20 \times 10^{-4}$	$7.14 \times 10^{-4}$	0.01

<sup>a</sup> Assumed barrier heights of *cis*-molecule. The observed heights are 230 cal/mol. <sup>b</sup>  $k_{rg}$  are the rate constants with rigid internal rotations of 1-bromopropene for all of *cis*- and *trans*-molecules and activated complex. <sup>c</sup>  $k_{rg}/k_{hin}$  represents the ratio of rate constant of the rigid to true hindered rotor.

tions of our calculation may require further experimental studies mainly due to the scarcity of data bases on elementary isomerizations of 1-halopropenes and the complexity of concurrent radical processes.<sup>20</sup>

The rate constants have decreased in general by allowing internal rotation and the degrees of these difference are strongly dependent on the model used in the approximation method. The rate constants with free rotor are nearly the same as those with the rigid internal rotation. The Pitzer rotor and true hindered rotor treatment show almost same results with each other. Since the Pitzer,  $R_{II}$ , and the true hindered internal rotor,  $R_{III}$ , are the overestimations of the free oscillator treatment, both treatments correspond to an ordinary interpretation of wave Eq. (7) except that solutions of the equation are somewhere between the free rotation and harmonic oscillator treatment.

As shown in Table 5, the rate constants are rather insensitive by free rotor treatment,  $R_I$ . These findings are attributed to the fact that the barrier height differences between the reactant and activated complex do not appear in rate constant formulation. This interpretation is further supported by observing the ratios of  $k_{rg}/k_{cis-1}$  and  $k_{rg}/k_{cis-2}$  in Table 6. The ratio,  $k_{rg}/k_{cis-1}$ , the rate constant ratio of the rigid internal rotor to that of the free internal rotor of *cis*-molecule, is almost same with that with true hindered rotations of *cis*, *trans* and activated complex,  $R_{III}$ , in Table 5. These are due to an unusually low potential barrier height of internal rotation of *cis*-1-bromopropene which is not so much different from a free rotation. Thus, *cis* molecule lying in low barrier height is nearly same as a rigid even if it is treated as a harmonic oscillator as shown in Table 6.

The temperature and pressure dependences between the

rigid and allowed systems are not so sensitive but show small increasing effect with temperature drop and an opposite effect with pressure increase. The pressure dependence may be well understood in terms of the contribution of the reverse reaction to the overall reaction rate. The barrier height difference between reactant and activated complex is greater in *cis*-1-bromopropene than in *trans* isomer. By pressure increase, the second term of denominator in Eq. (2) approaches zero and hence the contribution of the reverse reaction to the overall reaction becomes negligible compared to the case at low pressure. Consequently, the difference of the isomerization rate constants between rigid and allowed systems becomes larger.

The results from repeated calculation at various barrier heights of reactant molecule of *cis*-1-bromopropene, can offer a conclusive evidence about the internal rotation effects on *cis-trans* isomerization of 1-halopropenes as shown in Table 7, where an effect of the barrier heights difference between reactant and activated complex is demonstrated clearly. The decrease of the barrier heights difference between the reactant and activated complex brings smaller difference between the rate constants with rigid and allowed systems. The rate constants at both barriers of 2120 cal/mol for the product and the reactant molecules approach the values as those of rigid systems. At 2920 cal/mol of reactant barrier, the same value with that of activated complex, the rate coefficients of the rigid internal rotation system approach even closer the values of the rate coefficients of the allowed internal rotation of methyl group system. These studies indicate that the rate coefficient is extremely sensitive to the barrier height of the reactant and varies up to a maximum of three times depending on the barrier height models on *cis-trans* isomerization reaction of 1-halopropenes.

In *cis-trans* isomerization of an ethylenic compounds, the  $\pi$ -bond energy of c=c bond which generally defined as the difference between the bond dissociation energies for the successive breaking of two bonds of saturated compound may be closely connected with the activation energy of isomerization reaction. The relationships between the two at some several molecules are well explained in ref. 19. In 1-bromopropene system where the activation energy difference between *cis*- and *trans*-molecule,  $\Delta H_0^\circ$ , is not large, ca. 122.86 cal/mol, the difference between the isomerization rate coefficients of *cis*- and *trans*-system is governed mainly by the difference of internal rotation barrier heights. These findings are in good agreement with the experimental results<sup>20</sup> where the isomerization rate constants of *trans*-1-bromopropene are 2-3 times larger than those of *cis*-1-bromopropenes under an inhibited condition of radical process at temperatures from 620.8 to 753.2 K over the pressure range of 0.17-50.3 torr.

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## Two Crystal Structures of Ethylene and Acetylene Sorption Complexes of Dehydrated Fully Ca<sup>2+</sup>-Exchanged Zeolite A

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Two crystal structures of ethylene ( $a=12.272(2)$  Å) and acetylene ( $a=12.245(2)$  Å) sorption complexes of dehydrated fully Ca<sup>2+</sup>-exchanged zeolite A have been determined by single crystal X-ray diffraction techniques in the cubic space group, *Pm3m* at 21(1)°C. Their complexes were prepared by dehydration at 360°C and  $2 \times 10^{-6}$  Torr for 2 days, followed by exposure to 200 Torr of ethylene gas and 120 Torr of acetylene gas both at 24°C, respectively. The structures were refined to final *R* (weighted) indices of 0.062 with 209 reflections and 0.098 with 171 reflections, respectively, for which  $I > 3\sigma(I)$ . The structures indicate that all six Ca<sup>2+</sup> ions in the unit cell are associated with 6-oxygen ring of the aluminosilicate framework. Four of these extend somewhat into the large cavity where each is coordinated to three framework oxide ions and an ethylene molecule and/or an acetylene molecule. The carbon to carbon distance in ethylene sorption structure is 1.48(7) Å and that in acetylene sorption structure 1.25(8) Å. The distances between Ca<sup>2+</sup> ion and carbon atom are 2.87(5) Å in ethylene sorption structure and 2.95(7) Å in acetylene sorption structure. These bonds are relatively weak and probably formed by the electrostatic attractions between the bivalent Ca<sup>2+</sup> ions and the polarizable  $\pi$ -electron density of the ethylene and/or acetylene molecule.

### Introduction

Calcium exchanged zeolite A is very useful industrially for drying and purifying of natural gas, carbon dioxide removal, separation of *n*- and isoparaffine<sup>1</sup>, and detergent builder<sup>2</sup>.

Recently, the crystal structure of dehydrated fully Ca<sup>2+</sup>-exchanged zeolite A<sup>3</sup> and of their halogen sorption complexes have been determined<sup>3,4</sup> by single-crystal X-ray diffraction techniques. In these structures, six divalent cations are located on three different threefold axes associated with 6-ring oxygens. Dehydrated Ca<sup>2+</sup>-exchanged zeolite A sorbs *ca.* six

diiodine molecules at 80°C and also sorbs 6 dibromine molecules per unit cell at 24°C, respectively. The structural analyses indicate that each halogen molecule forms a charge transfer complex with framework oxygen ( $\text{I-I-O} = 180(2)^\circ$ ,  $\text{Br-Br-O} = 178(2)^\circ$ ,  $\text{I-I} = 2.72(2)$  Å,  $\text{Br-Br} = 2.64(9)$  Å,  $\text{I-O} = 3.32(3)$  Å, and  $\text{Br-O} = 3.12(7)$  Å)<sup>3,4</sup>.

Several ethylene and acetylene sorption structures of transition metal ion exchanged zeolite A have been studied. In the structures of dehydrated Co<sub>4</sub>Na<sub>4</sub>-A<sup>5</sup> and Mn<sub>4</sub>Na<sub>4</sub>-A<sup>6</sup>, the transition metal ions adopt positions close to the anionic zeolite framework where they achieve near-trigonal planar coord-