Gas Phase Thermal *cis-trans* Isomerization Reaction of 1-Bromopropene

Do Sung Huh, Jae Young Um, Sun Jin Yun, Kwang Yul Choo†, and Kyung-Hoon Jung*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-650
†Department of Chemistry, Seoul National University, Seoul 151-742. *Received April 25, 1990*

The kinetics of thermal *cis-trans* isomerization reaction of 1-bromopropene(1-BP) was studied at temperatures from 620.8 to 753.15 K over the pressure range 0.17-50.3 Torr. Both the inhibition effect by cyclohexene or propene and the catalytic effect by HBr showed a radical process as the main mechanism of the isomerization. In the suppression of the radical process by the inhibitors, the molecular process also contributed to overall reaction rate. The reactions demonstrated the first order kinetics under both uninhibited and inhibited conditions and could be represented by the expressions (R = 1.987 cal/mol/K)

$$k_{un}/s^{-1} = (3.45 \pm 1.50) \times 10^{11} \exp[(-48100 \pm 2000)/RT]$$

$$k_{inh}/s^{-1} = (2.98 \pm 1.40) \times 10^{12} \exp[(-55800 \pm 1800)/RT]$$

where k_{un} is the observed rate constant of *cis*-1-bromopropene(1-BP_c) to *trans*-1-bromopropene(1-BP_t) under uninhibited condition at initial pressure of 50 Torr and k_{inh} is the rate constant under maximal inhibition by cyclohexene.

The ratio of rate constants for bromine atom elimination from the allylic hydrogen of reactant(1-BP) and from the inhibitors, propene and cyclohexene, were measured from the observed rates of the uninhibited and inhibited reactions. The inhibition efficiencies of cyclohexene and propene were compared kinetically from the rate constants and shown to give good agreement with the previous results reported from other alkyl bromide pyrolyses.

Introduction

The gas phase thermal *cis-trans* isomerization reactions of 2-butene[1-3] and substituted ethylenes[4-10] hve been studied extensively by several authors. The reactions have shown a tendency to proceed by a homogeneous unimolecular mechanism at low pressure, while at high pressure the reactions have not shown this tendency but occur by a rather complex radical mechanism. For example, the isomerization reactions of *cis*-2-butene[1] and *trans*-ethylene-d_2[4] have shown unimolecular characteristics in low pressure region, whereas at high pressure the reactions have not followed a homogeneous unimolecular behavior. These complications of butene and substituted ethylene systems at high pressure have been resolved[5-7] as radical processes, possible heterogeneous reactions, and unimolecular contribution to the isomerizations.

Very little data exist on the isomerization of 1-halopropene,[11,12] though *cis-trans* isomerization of other substituted ethylenes have been studied extensively. The fact that 1-BP has both allylic hydrogens and bromine atom attracted our interest to study the *cis-trans* isomerization of 1-BP in the gas phase since bromine atom is able to catalyse the isomerization and can be eliminated simultaneously by the reaction of Br atom with allylic-hydrogen in a radical process. With regard to the inhibition effect of allylic compounds by bromine atom, studies about the relative efficiency of inhibitors have been reported on pyrolyses of *n*-propylbromide,[13] *n*-butylbromide,[14] and 1,2-dibromopropane systems.[15]

In the present work, *cis-trans* isomerization of 1-bromopropene was studied in the gas phase to obtain informations on the inhibition effect of allylic compounds for radical processes by bromine atoms. The relative rate constants of the allylic hydrogen abstraction by bromine were obtained for the inhibitors, propene and cyclohexene, by comparing the observed uninhibited and inhibited rate constants of the *cis-trans* isomerization reaction of 1-BP.

Experimental

Apparatus. A conventional high-vacuum static system was employed. The reaction vessel was cylindrical quartz tubing with a volume of 296 cm^3 and surface-to-volume ratio (s/v) of *ca.* 1.0 cm^{-1}. The inner surface of the vessel was coated with carbon film by pyrolysing allyl bromide for 48 hrs at 750 K and at 200 Torr. Heating of the reactor was done with a tubular furnace (Electroglas). The temperature of the furnace was controlled to within ±1.0 °C along the length of the furnace by an internal thermocouple. The reaction temperature was calibrated with a digital HP3465B multimeter using a K-type thermocouple and a water-ice junction. Temperature fluctuations in the reaction vessel were kept to less than ±0.5 °C.

The experiments were carried out at 620.8-746.15 K in the pressure range of 0.17 to 50.3 Torr. Pressure measurements for both reactant and the additives were made using capacitance gauges, Setra Model 239 Pressure Transducer for below 10 Torr and Setra Model 280 E for above 10 Torr.

Product analysis was done using the gas chromatographic technique by comparing their retention times and peak areas with those of authentic samples. The gas chromatograph used in this work was a two-stage home-made isothermal instrument equipped with a single hydrogen flame ionization detector and a Hewlett-Packard 3380 A integrator. Sample separation was achieved by 60 m × 0.75 mm ID VOCOL wide bore glass capillary column, Supelco, at 35 °C with a nitrogen carrier gas flow rate of 6.8 $cm^3 \cdot min^{-1}$ and 15 $cm^3 \cdot min^{-1}$ of make-up gas. Mass spectrometry was done to confirm some of the products using an HP 5985B gas chromatograph/mass

*Author to whom correspondence should be addressed.

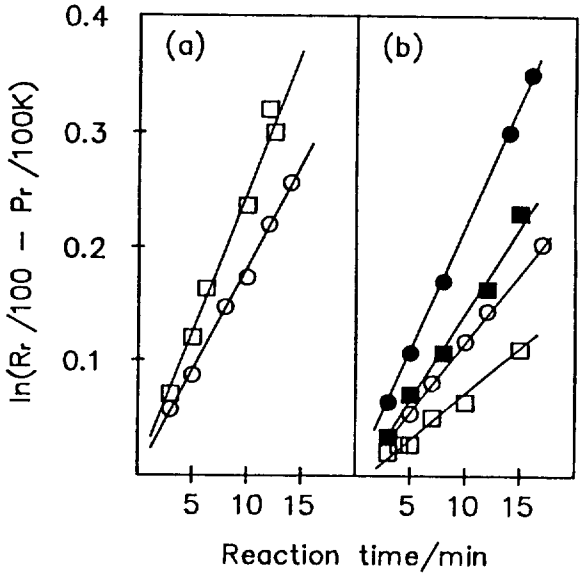


Figure 1. First-order plot: (a) under uninhibited conditions of 1-BP at 50.0±1.0 Torr and at 677.3 K: □ and ○ represent 1-BP_t and 1-BP_c as starting materials; and (b) under inhibited conditions of 1-BP and at same pressures of the reactant and the inhibitor, 10.0±0.1 Torr and at 718.4 K for 1-BP_t, 729.7 K for 1-BP_c: ●, 1-BP_c and propylene; ■, 1-BP_t and propylene; ○, 1-BP_c and cyclohexene; □, 1-BP_t and cyclohexene as starting materials.

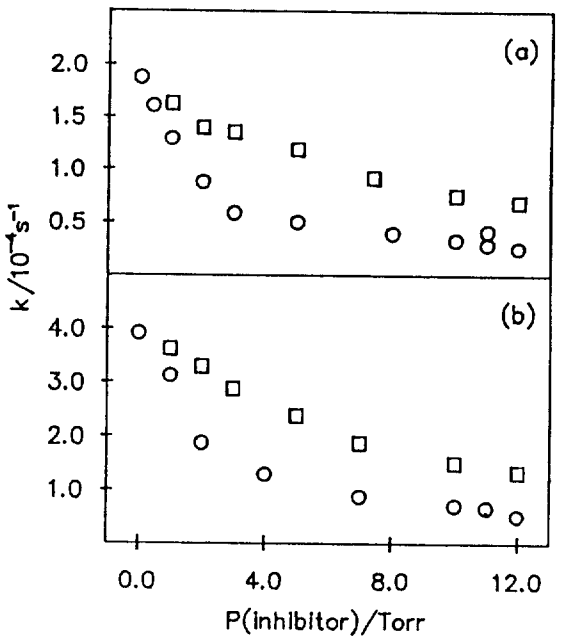


Figure 2. Isomerization rate constants of 1-BP at 10.0±0.1 Torr and at 718.4 K with inhibitor pressure change; ○, cyclohexene; □, propylene as an inhibitor. (a) for 1-BP_c and (b) for 1-BP_t as starting materials. The equilibrium constant for *cis* – *trans* isomerization was 0.52.

spectrometer.

Materials. 1-BP(an isomeric mixture of *cis* and *trans*), 2-bromopropene, 3-bromo-propene, benzene, and cyclohexene, obtained from Aldrich Chemicals and with stated purities of 98, 99, 99, 99, and 99%, respectively, were used after trap-to-trap distillation at 77 K. *cis* – 1-Bromopropene was separated from the *trans* isomer by gas chromatograph using a 20% OV-17, 1/4 in. ×3 m s.s. column. Propylene and hydrogen bromide, stated purities 99 and 99.8% obtained from Matheson, were purified by low temperature trap-to-trap distillation.

Results

In the reaction of 1-BP at 620.8–746.2 K and at 0.17–50.3 Torr using 1-BP_c or 1-BP_t as starting materal, the *cis* – *trans* isomerization was a major reaction. Propylene, allylbromide and benzene were observed as minor side products. The isomerization was significantly decreased by adding inhibitors, and the side products were completely suppressed.

The reaction was demonstrated to follow the first-order reversible kinetics under both uninhibited and inhibited conditions as shown in Figure 1. The rate constants were calculated from the expression, $\ln(R_t/100\text{–}P_t/100\ \mathrm{K}) = -k_f(\frac{k+1}{k})t$, where R_t and P_t are the percentages of the isomers remaining and formed after time t; K, the equilibrium constant for the process of *cis* – *trans* isomerization($= k_f/k_b$); and k_f and k_b, the first-order rate constants for the foward and reverse reactions, respectively. The equilibrium constant, K, was obtained from $\log(1/\mathrm{K}) = 0.15 + 96.4/(\mathrm{T} + 273.15)$.[12,17]

The inhibition effects by cyclohexene or propylene was studied and displayed in Figure 2 as a function of inhibitor concentration.

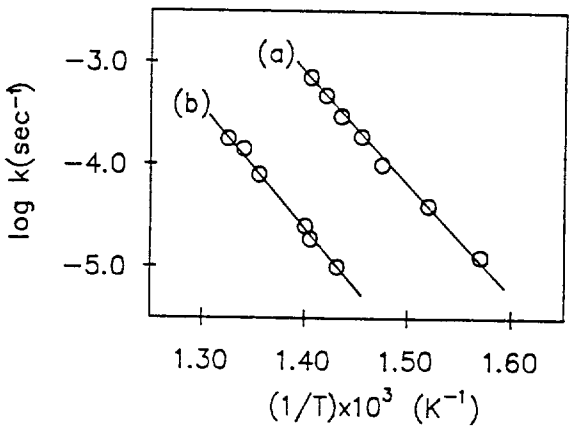


Figure 3. Temperature dependence of *cis* to *trans* isomerization rate constant at temperatures from 637.2 to 753.2 K: (a) under uninhibited conditions at 50.0±1.0 Torr; (b) under inhibited by cyclohexene at both 3.0±0.1 Torr of 1-BP_c and cyclohexene.

Temperature dependencies of the rate of *cis* – *trans* isomerization were studied in the range of 637.2 to 753.2 K at 50 Torr for uninhibited condition and at 3 Torr for inhibited condition by cyclohexene, and displayed in Figure 3 and the Arrhenius parameters are given in Table 1. The frequency factor and activation energy under inhibited condition were higher than the values under uninhibited condition, in contrast to the general trend that the activation energy for the unimolecular thermal reaction generally increases[16] with pressure. These observations show that the *cis* – *trans* isomerization reaction of 1-BP would proceed by dual mechanism, *i.e.*, a radical and a molecular processes.

As predicted from the equilibrium constant, the reactivity

Table 1. Arrhenius Parameters for the Formation of *trans*-Bromopropene

	Un	Inhib
log A (s^{-1})	11.54	12.47
E_a (kcal·mol^{-1})	48.1	55.8

Un: at 50 Torr in uninhibited condition.
Inhib: at 3 Torr in inhibited condition by cyclohexene.

Table 2. Arrhenius Parameters for Thermal *cis-trans* Isomerization Reactions of Various Substituted Ethylenes

Reactants	log A(s^{-1})	E_a (kcal·mol^{-1})	Ref.
cis-$CH_3CH=CHCH_3$	13.79	62.8	1
	14.0	62.4	2
	13.4	61.6	9
trans-CHD=CHD	13.0	65.0	4
cis-CHCl=CHCl	12.76	56.0	5
trans-CHCl=CHCl	12.68	55.3	5
cis-$CH_3CH=CHCOOCH_3$	13.2	57.8	6
cis-$CH_3CH=CHCN$	11.0	51.3	7
cis-$CH_3CH=CHD$	13.16	61.3	8
cis-CHF=CHF	13.2	62.8	9
cis-$C_6H_5CH=CHCN$	11.6	46.0	10
cis-$CH_3CH=CHBr$	12.5	55.8	This Work

of 1-BP_t was higher than that of 1-BP_c by a factor of *ca.* 2 in the same condition as shwon in Figure 2. Propylene, allylbromide, and benzene in 1-BP_t system were also observed as minor side products as observed from 1-BP_c.

The catalytic effects in the presences of HBr and O_2 were found to be very effective not only to the isomerization but also to the side reactions including positional isomerization.

Discussions

The thermal *cis-trans* isomerization of 1-BP was demonstrated to follow the first-order reversible kinetics under both uninhibited and inhibited conditions as stated in the results. The first order rate constant under uninhibited condition increased rapidly with reactant pressure rise. This result shows that a radical process plays a significant role for the isomerization and obeys also a first-order reaction kinetics(*vide infra*). The order of the reaction under inhibited condition was not changed at high pressure but the magnitude of the first-order rate constant was decreased considerably. Since the molecular process is first-order and the molecular isomerization rate constants of other substituted ethylenes are similar to this inhibited isomerization rate constant as shown in Table 2, the first-order rate constant obtained in the experiment can be expressed as a sum of these two first-order rate constants, *i.e.*, the molecular and the radical processes.

For the radical process, then, we propose a consecutive-step mechanism involving Br atom addition to the π-bond where bromine atom is produced by the initiation process whereby 1-BP molecule decomposes into allyl radical and bromine atom.

$$CH_3-CH=CHBr \xrightarrow{k_i} CH_2=CH-\dot{C}H_2+Br$$

$$Br+cis-CH_3CH=CHBr \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} c-CH_3CHBr-\dot{C}HBr \quad (1)$$

$$c-CH_3CHBr-\dot{C}HBr \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} t-CH_3CHBr-\dot{C}HBr \quad (2)$$

$$t-CH_3CHBr-\dot{C}HBr \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} trans-CH_3CH=CHBr+Br \quad (3)$$

The dissociation in reaction (*i*) by 1,3-hydrogen shift may be interpreted in terms of the relative stability of allyl radical ($\Delta H_f^0 = 40.6$ kcal/mol)[18] comparing with vinyl radical ($\Delta H_f^0 = 69 \pm 2$ kcal/mol).[18] Such shift has been observed previously in the gas phase.[19] The letters *c* and *t* in reactions (1), (2), and (3) mean the $C_3H_5Br_2$ radical from the *cis*-1-BP and *trans*-1-BP by the addition of bromine atom. The transient structure for the initiation may be approximated by the hyperconjugated structure suggested by Beaudet.[20] Activation energy difference for initiation process between 1-BP_c and 1-BP_t systems may be small and the *trans* isomer would have lower activation energy since it is free from a nonbonded interaction[20] between the bromine atom and methylhydrogens.

The bromine atom can be eliminated by abstracting allylic hydrogen from 1-BP or inhibitors through reaction (t) or (I) and also can be terminated by recombination (4) and disproportionation reactions (5).

$$CH_3CH=CHBr+Br \xrightarrow{k_t} \dot{C}H_2CH=CHBr+HBr \quad (t)$$

$$In-H+Br \xrightarrow{k_{Ix}} \dot{I}n+HBr \quad (I)$$

$$Br+Br+M \xrightarrow{k_4} Br_2+M \quad (4)$$

$$Br+\dot{C}H_2CH=CHBr \xrightarrow{k_5} CH_2=C=CHBr+HBr \quad (5)$$

where In-H represents an inhibitor and the subscript *Ix* of k_{Ix} for inhibitor *x*. The suffix *x* of *Ix* denotes *x* inhibitor, *e.g.*, cyclohexene or propene.

From reactions (1)-(5), the rate of appearance of 1-BP_t due to radical process can then be formulated by applying the steady-state approximation to the intermediate species, *i.e.*, Br, c-$C_3H_5Br_2$, and *t*-$C_3H_5Br_2$, and neglecting steps (4) and (5), since $k_4[Br]^2$ and $k_5[Br][C_3H_4Br]$ are very small.

$$\frac{d[1-BP_t]}{dt} = k_3[t-C_3H_5Br]-k_{-3}[1-BP_t][Br]$$

$$=\left[\frac{k_1k_2k_3}{k_2k_3+k_{-1}k_3+k_{-1}k_{-2}}\right]\left[\frac{k_i}{k_t+k_{Ix}\dfrac{[In-H]}{[1-BP]}}\right][1-BP_c]$$

$$-\left[\frac{k_{-1}k_{-2}k_{-3}}{k_2k_3+k_{-1}k_3+k_{-1}k_{-2}}\right]\left[\frac{k_i}{k_t+k_{Ix}\dfrac{[In-H]}{[1-BP]}}\right][1-BP_t]$$

The neglection of reactions (4) and (5) for the derivation of eqn. (i) was justified by the known kinetic information.

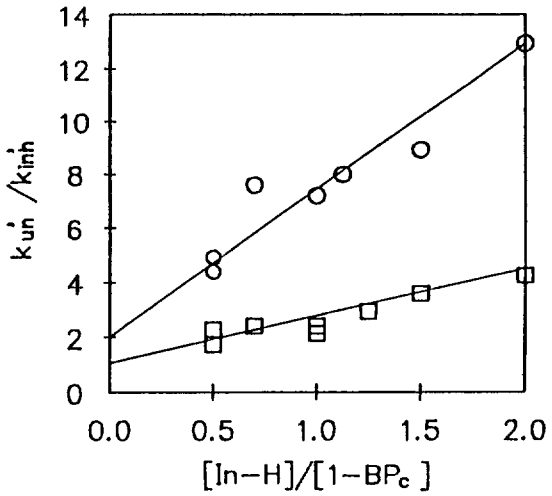


Figure 4. Isomerization rate constant ratio of uninhibited to inhibited of 1-BP$_c$ at 50.0 ± 1.0 Torr and at 712.3 K with inhibitor pressure change: ○, cyclohexene; □, propylene as an inhibitor.

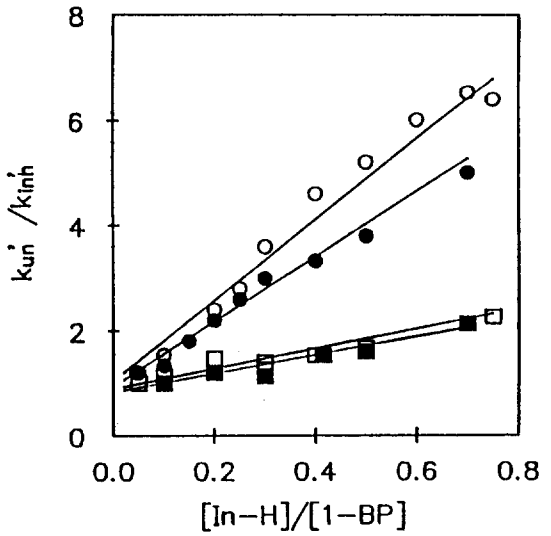


Figure 5. Isomerization rate constant ratio of uninhibited to inhibited of 1-BP at 10.0 ± 0.1 Torr and at 718.4 K with inhibitor pressure change: ○, 1-BP$_c$ and cyclohexene; ●, 1-BP$_t$ and cyclohexene; □, 1-BP$_c$ and propylene; ■, 1-BP$_t$ and propylene as starting materials.

The recombination rate constant k_4 is known to be $\log(k_4/cm^3mol^{-1}s^{-1}) = 8.5 + (2.4/\theta)$[21], where θ represents 2.303 RT and the value of k_5 has an estimated value of *ca.* 10^{12} $cm^3 \cdot mol^{-1}s^{-1}$ from similar disproportionation studies.[22] The rate constant for hydrogen abstraction by bromine atoms from propene is known to be $\log(k_{1X}/cm^3mol^{-1}s^{-1}) = 12.1 - (3.5/\theta)$.[22] Thus if we assume that the Br atom concentration has a value within about 1% of the reactant concentration in our reaction conditions, the value of $k_4[Br]^2$ and $k_5[Br][C_3H_4Br]$ are negligibly small in comparison to k_t[1-BP][Br] or k_{1X}[In-H][Br]. The allylic radical, C_3H_4Br, produced in reaction (t) is stable and thus can be terminated by increasing the carbonaceous deposition or producing allylbromide and benzene.

The first and second terms in eqn. (i) represent the forward and backward reaction in the reversible *cis-trans* isomerizaon of 1-BP due to radical process. This equation establishes the first-order kinetics of the isomerization due to radical process also. Then, the forward first-order rate constant due solely to radical process can be rewritten from eqn. (i)

$$k_{f.\,rad} = \left[\frac{k_1 k_2 k_3}{k_2 k_3 + k_{-1} k_3 + k_{-1} k_{-2}}\right]\left[\frac{1}{1+\dfrac{k_{1x}[\text{In}-\text{H}]}{k_t[1-BP]}}\right]\left[\frac{k_t}{k_t}\right] \quad \text{(ii)}$$

where $k_{f.rad}$ represents the forward first-order rate constant for the radical process. The second bracket in eqn. (ii) signifies the inhibition effect where the rate constant under inhibited condition decreases as the inhibitor concentration [In-H] increase. Hence, the effect is greater for an inhibitor with a higher inhibiton rate constant k_{1X}. The forward rate constant due to molecular process, *i.e.*, $k_{f.mol}$, would not be affected by the addition of inhibitor. The $k_{f.rad}$ was obtained by eliminating the $k_{f.mol}$ from the observed forward first-order rate constant. The fully inhibited rate constant at 3 Torr was used for the $k_{f.mol}$. The pressure dependent molecular process is ignored since the increase of rate constant by pressure increase is greater than previous molecular isomerization reaction.[16] This means that the radical processes rapidly increase with pressure in this isomerization, and thus the uninhibited reaction at 50 Torr has been compared with the fully inhibited one at 3 Torr. The ratio of uninhibited to inhibited rate constant of $k_{f.rad}$ is expressed from eqn. (ii)

$$\frac{k'_{un}}{k'_{inh}} = 1 + \frac{k_{1x}[\text{In}+\text{H}]}{k_t[1-BP]} \quad \text{(iii)}$$

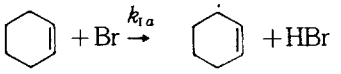
where k'_{inh} and k'_{un} represent $k_{f.rad}$ at inhibited and uninhibited conditions by radical process only. Hence the observed k_{inh} and k_{un} are $k_{inh} = k'_{inh} + k_{f.mol}$ and $k_{un} = k'_{un} + k_{f.mol}$, respectively. The ratio varies linearly with the concentration ratio of inhibitor to reactant, *i.e.*, [In-H]/[1-BP], and the slope is k_{1X}/k_t. From the slope the inhibition efficiency of inhibitor is obtained. The results are shown in Figures 4 and 5. As shown in Figures 4 and 5, the slope for cyclohexene is higher than that of propene for either reactants, *i.e.*, 1-BP$_c$ or 1-BP$_t$. The difference of the slope between *cis* and *trans* is comparable to the experimental error for both cyclohexene and propene. The maximum inhibited rate constant of the isomerization was *ca.* 1/5 times that of the uninhibited for cyclohexene and *ca.* 1/2.5 times for propene at 10 Torr of reactant pressure. At 50 Torr, the inhibited rate constant reduced to 1/10 times that of the uninhibited for cyclohexene. The ratios k_{1_a}/k_t for cyclohexene inhibitor and k_{1_b}/k_t for propene are listed in Table 3. Table 3 shows relative reactivity of allylic hydrogen for 1-BP, propene, and cyclohexene toward the abstraction by hydrogen by bromine atom. Using the Arrhenius parameters of k_{1_b} by Benson *et al.*[22] where $\log(k_{1_b}/cm^3mol^{-1}s^{-1}) = 12.1 - 3.5/\theta$ for linear transition state, $\log(k_{1_b}/cm^3mol^{-1}s^{-1}) = 12.7 - 4.4/\theta$ for bent transition state, and k_{1_a}/k_t, and k_{1_b}/k_t of present study, the Arrhenius parameters of k_{1_a} and k_t are also estimated. The relative inhibition efficiency of cyclohexene to propene is obtained from the ratio of $k_{1_a}/k_{s_{1_b}}$. Here, we rewrite the equations for the rate constants, k_t, k_{1_a}, and k_{1_b}, for comparison between inhibitors.

$$CH_3CH{=}CHBr + Br \xrightarrow{k_t} \dot{C}H_2CH{=}CHBr + HBr \quad \text{(t)}$$

Table 3. The Ratios of Abstracting Rate Constants for Allylic Hydrogen of Cyclohexene, Propene, and 1-BP by Bromine Atom

Reactants		k_{1_a}/k_t	k_{1_b}/k_t	k_{1_a}/k_{1_b}
1-BP_c	*A*	7.2±0.5	1.8±0.2	4.0±0.5
	B	5.3±0.5	1.5±0.2	3.5±0.5
1-BP_t	*C*	6.2±0.5	1.6±0.2	3.9±0.5

A, *C*: The initial reactant pressure at 10 Torr and the reaction temperature at 718.4 K. *B*: The initial reactant pressure at 50 Torr and the reaction temperature at 712.3 K.



(6a) (≡I)

$$CH_3CH{=}CH_2 + Br \xrightarrow{k_{1b}} \dot{C}H_2CH{=}CH_2 + HBr \quad (6b)\ (\equiv I)$$

The ratio 4.0±0.5 of inhibition efficiency between propane and cyclohexene obtained in this study is similar to the reported value *ca.* 4-6 calculated in the pyrolyses of *n*-propylbromide,[13] *n*-butylbromide,[14] and 1,2-dibromopropane.[15]

From the foregoing discussion, $k_{f,rad}$ of eqn. (ii)for uninhibited reaction conditions is then reduced to

$$k_{un}' = \left[\frac{k_1 k_2 k_3}{k_2 k_3 + k_{-1} k_3 + k_{-1} k_{-2}}\right]\left[\frac{k_i}{k_t}\right]$$

$$\simeq \left[\frac{k_1}{1 + k_{-1}/k_2 + k_{-2}/k_2}\right]\left[\frac{k_i}{k_t}\right] \quad \text{(iv)}$$

where k_3 is assumed to be the same value of k_{-1}. The rate constant k_{-1} of eqn. (iv) has a value much less than the internal rotation rate constant k_2.[22] The ratio k_{-2}/k_2 has a value not much different to the inverse of equilibrium constant of *cis-trans* isomerization, *ca.* 2 at 637 K.[12] Then, eqn. (iv) reduces to.

$$k_{un}' \simeq \left[\frac{k_i}{3}\right]\left[\frac{k_1}{k_t}\right] \quad \text{(v)}$$

The initiation rate constant k_i can thus be estimated from the observed isomerization rate constant k_{un}' and the addition-abstraction rate constant ratio of 1-BP for bormine atom. Though the ratio k_1/k_t for 1-BP is not known, the ratio can not be less than 1.0 since Br atom adds rapidly to double bonds.[24] The A factor of k_i depends on the addition rate constant and the abstraction rate constant of 1-BP for bromine atom. A reasonable activation energy of k_i should be smaller than that of vinylbromide system, 60±5 kcal·mol^{-1},[25] and higher than the allylbromide system, 47.5 kcal·mol^{-1}.[26] From the activation energy for k_1, *ca.* 0 kcal·mol^{-1},[18,24] and k_t, 3-4 kcal·mol^{-1},[22] we obtain an activation energy of 54±5 kcal·mol^{-1}, for the initiation reaction.

Acknowledgement. This work was carried out with financial assistance from the Korea Science and Engineering Foundation and by the Basic Science Research Institute Program, Ministry of Education, 1990, Project No. BSRI-90-311 which we greatfully acknowledge.

References

1. B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959).
2. R. B. Cundal and T. F. Palmer, *Trans. Faraday. Soc.*, **57**, 1936 (1961).
3. C. Richard, A. Boiveaut, and R. Martin, *Intl. J. Chem. Kinet.*, **12**, 921 (1980).
4. J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).
5. L. D. Hawton and G. D. Semeluk, *Can. J. Chem.*, **44**, 2143 (1966).
6. J. N. Butler and J. Small, *Can. J. Chem.*, **41**, 2492 (1963).
7. J. N. Butler and. R. D. Mcalpine, *Can. J. Chem.*, **41**, 2487 (1963).
8. M. C. Flowers and N. Jonathan, *J. Chem. Phys.*, **50**, 2805 (1969).
9. P. M. Jeffers and W. Shaub, *J. Am. Chem. Soc.*, **91**, 7706 (1969).
10. G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **58**, 2428 (1936).
11. K. E. Harwell and L. F. Hatch, *J. Am. Chem. Soc.*, **77**, 1682 (1955).
12. K. G. Sharonov and N. M. Rozhnov, Izv. Vyssh. Ucheb. Zaved, *Khim. Khim. Tekhnol.*, **14**, 577 (1971).
13. A. Maccoll and P. J. Thomas, *J. Chem. Soc.*, 5033 (1957).
14. M. R. Bridge and J. L. Holmes, *J. Chem. Soc.*, B, 1008 (1967).
15. K.-H. Jung, S. J. Yun, and D. S. Huh, *J. Chem. Soc., Faraday Transact. II.*, **83**, 971 (1987).
16. P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Academic Press, London, 1973.
17. J. Lielmezes and H. Aleman, *Thermochim. Acta*, **10**, 333 (1974).
18. S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.
19. J. W. Wilt, in "Free Radicals", Vol I, J. K. Kochi, ed., John Wiley & Sons, 1973, p. 379.
20. R. A. Beaudet, *J. Chem. Phys.*, **40**, 2705 (1964).
21. M. L. Poutsma, in ref. 19, p. 202.
22. O. Kondo, R. M. Marshall, and S. W. Benson, *Intl. J. Chem. Kinet.*, **20**, 297 (1988).
23. S. W. Benson, K. W. Egger, and D. M. Golden, *J. Am. Chem. Soc.*, **87**, 468 (1965).
24. P. I. Abell, in ref. 19, Chapt. 13.
25. V. S. Rao and G. B. Skinner, *J. Phys. Chem.*, **92**, 6313 (1988).
26. H. Edward O'Neal and S. W. Benson, in ref. 19, p. 294.