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A Gas Phase Kinetic Study on the Thermal Decomposition of ClCH$_2$CH$_2$CH$_2$Br
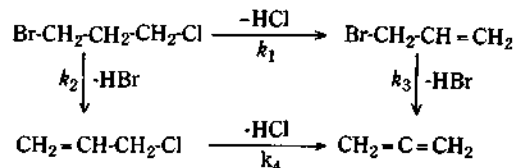
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The gas phase thermal decomposition of 1-bromo-3-chloropropane in the presence of radical inhibitor was studied by using the conventional static system. The mechanism of unimolecular elimination channel is shown below.

$$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Cl \xrightarrow[k_1]{-HCl} Br\text{-}CH_2\text{-}CH=CH_2$$

$$k_2 \downarrow -HBr \qquad\qquad k_3 \downarrow -HBr$$

$$CH_2=CH\text{-}CH_2\text{-}Cl \xrightarrow[k_4]{\cdot HCl} CH_2\text{-}C=CH_2$$

In this scheme, the total molecular dissociation rate constant, $(k_1 + k_2)$, for the decomposition of BrCH$_2$CH$_2$CH$_2$Cl was determined by pyrolyzing the BrCH$_2$CH$_2$CH$_2$Cl in the temperature range of 380-420 °C and in the pressure range of 10~100 torr. To obtain k_3 and k_4, and to obtain k_1 and k_2 independently, the thermal decompositions of allyl chloride and allyl bromide were also studied. The Arrhenius parameters for each step are as follows;

$\log A_\infty = 14.20(\sec^{-1})$, $E_a = 56.10(\text{kcal/mol})$ for reaction path 1;

$\log A_\infty = 12.54(\sec^{-1})$, $E_a = 49.75(\text{kcal/mol})$ for reaction path 2;

$\log A_\infty = 13.41(\sec^{-1})$, $E_a = 50.04(\text{kcal/mol})$ for reaction path 3;

$\log A_\infty = 12.43(\sec^{-1})$, $E_a = 52.78(\text{kcal/mol})$ for reaction path 4;

Finally, the experimentally observed pressure dependence of the rate constants in each step is compared with the theoretically predicted values that are obtained by the RRKM calculations.

Introduction

The thermal decomposition reaction of alkyl halides has been studied since Glass and Hinselwood's first report was published in 1929[1]. The main processes are classified into three mechanisms; first, a direct unimolecular elimination of hydrogen halide, second, a breaking of the carbon-halogen bond yielding a halogen atom, and third, the halogen atom participate in the propagation of long chain, *i.e.*, radical chain reaction[2].

Maccoll reported that the thermal decomposition of allyl bromide in the temperature range of 320-380 °C was homogeneous and first order, involving the elimination of bromine atom, with rate constant $k = 2.11 \times 10^{12} \exp(-45,500/RT)$ sec^{-1}[2]. In the unimolecular elimination reactions, the high pressure Arrhenius parameters of 1-bromopropane were reported to be; $\log A = 12.8$-$13.2(\sec^{-1})$, $E_a = 50.7$-51.9(kcal/mol) [3-5]; that of 2-bromopropane; $\log A = 13.6$-$13.7(\sec^{-1})$, $E_a = 47.6$-47.8 (kcal/mol) [5-7]; that of 1-chloropropane; $\log A = 13.5(\sec^{-1})$, $E_a = 55.0$ (kcal/mol) [8]; that of 2-chloropropane; $\log A = 11.0$-13.6 (sec^{-1}), $E_a = 42.4$-50.5 (kcal/mol) [9,10].

The study of the unimolecular elimination reactions of dihalocompounds was also carried out by some workers. Young *et al.* reported that the Arrhenius parameters for the unimolecular decompositions of 2,2-dichlorobutane and 2,2-dichloropropane were $E_a = 50.2, 51.4$(kcal/mol) and $\log A =$ 14.49, 14.52(sec^{-1}) respectively[11]. Holbrook and Parry reported that the 1,2-dichloropropane pyrolysed more slowly than the 1,1-dichloropropane and the former produced more cis : trans product ratios than the latter did[12]. The rate constant for the unimolecular elimination reaction of 1,2-dichloropropane was reported to be $\log A = 13.70$ sec^{-1}, and $E_a = 54.9$(kcal/mol)[13,14].

It would be interesting to investigate the reaction for the thermal decomposition of dihalocompounds which have two different halogen atoms at different positions. The present paper describes the unimolecular elimination reaction of dihalocompounds, especially for 1-bromo-3-chloropropane. This reaction is considered to proceed via two reaction channels, HCl and HBr elimination.

The pyrolysis of 1-bromo-3-chloropropane in our conventional static system was carried out in the temperature range of 380-420 °C and the decomposition reaction in the presence of free radical inhibitors was found to be homogeneous and first order unimolecular elimination reaction. In this work, toluene (in case of 1-bromo-3-chloropropane) and butene (in case of allyl bromide and allyl chloride) were used to inhibit the unwanted radical-reaction.

The pressure dependence of the rate constants of allyl chloride and 1-bromo-3-chloropropane was also studied. The Rice-Ramsperger-Kassel-Marcus (RRKM) unimolecular rate theory was compared with experimental data for the pressure dependence.

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Experimental

Material. Allyl chloride(m.p. -134.5 °C, b.p. 45 °C (760 atm)), allyl bromide(m.p. -119.4 °C, b.p. 70 °C (753 atm)) and 1-bromo-3-chloropropane(m.p. -58.87 °C, b.p. 143.36 °C (760 atm)) were obtained commercially (Aldrich, 99%) and tested for impurities by gas chromatography(GC) after several freeze-pump-thaw cycles.

Toluene and cis-Butene-2 (Matheson) after several freeze-pump-thaw cycles were used as radical scavenger.

Apparatus. Our conventional static pyrolysis system is shown in our previous publications[14]. The reactor was made of quartz tube with 57 mm diameter and 286.5 cc volume. The pressure in the reactor was read by the electronic pressure transducer (Validyne, Model CD 223). The temperature of the reactor was controlled constantly by using the furnace (Fisher, Model 1012) connected with the feed-back temperature controller (Hanna) and the voltage transformer (Sanya). It was read by the digital temperature convertor (Omega, Model 2176A) connected with the chromel-alumel thermocouples (Omega, K type). The FID (flame ionization detector) was used as a GC detector and Ar as the carrier gas. The GC column was Hall M-18-OL(2.4 m).
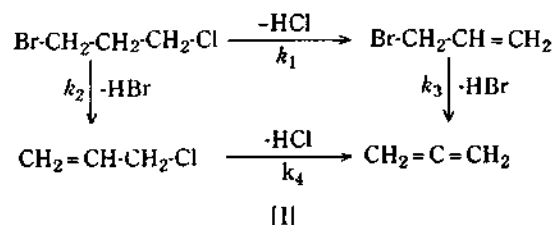
Analyses of the reaction product were carried out by monitoring the GC retention times and the intensities of the GC peaks. The intensities *vs.* the concentrations of reactants and products were calibrated by comparing those of authentic samples.

Experimental Procedure. Samples had been decomposed several times to season the surface of reactor for homogeneous reaction before the rate constants were measured. Then samples and inhibitors were mixed in the reservoir and they were injected into reactor at a specified temperature.

The extent of the decompositions was monitored by injecting small portion of the reactant into GC through the 6 port GC sampling valve. Intervals of injection were 400-1000 seconds depending on the kind of samples and the reaction temperatures. Corrections for injecting portion (about 2% of reactant concentration) to the reactant concentration were also carried out. Rate constants were measured by analyzing the quantity of samples as a function of the reaction time. The rate constants were obtained from the slope of the ln[reactant] versus the reaction time plot.

Results and Discussion

The reaction paths for the decomposition of 1-bromo-3-chloropropane under the conditions of negligible radical chain reactions are supposed to follow the scheme as shown below [I]:

$$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Cl \xrightarrow[k_1]{-HCl} Br\text{-}CH_2\text{-}CH = CH_2$$

$$k_2 \downarrow -HBr \qquad\qquad k_3 \downarrow -HBr$$

$$CH_2 = CH\text{-}CH_2\text{-}Cl \xrightarrow[k_4]{-HCl} CH_2 = C = CH_2$$

[I]

To obtain rate constants and Arrhenius parameters of each reaction path, three series of experiments were carried
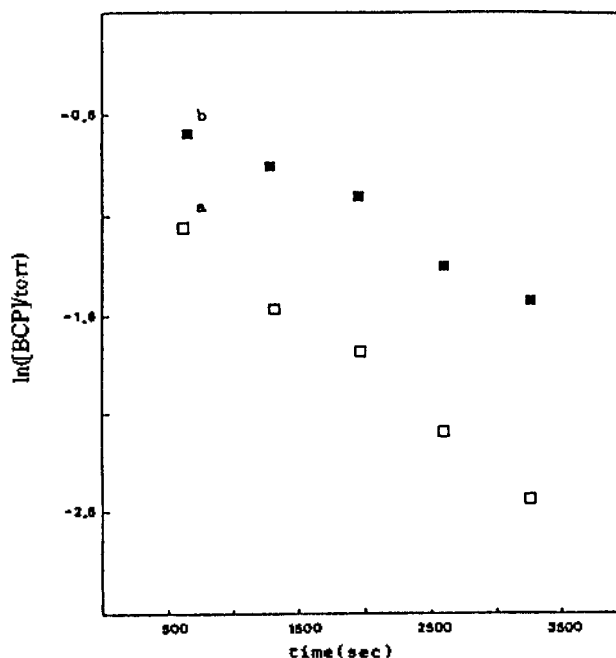

Figure 1. ·Effect of added Toluene for 1-bromo-3-chloropropane (BCP) decomposition. a : Total pressure 17.7 torr at 400 °C. b : Total Pressure 36 torr, Toluene/[BCP] = 0.5 at 400 °C.

Table 1. Effect of Added Radical Inhibitors

Samples	T(°C)	P (Torr)			$k(10^{-4})sec^{-1}$
		sample(S:I)	argon	total	
Allyl	370	1.43(1:1)	52.07	53.50	2.57
Bromide		0.87(1:3)	16.96	17.83	2.63
		7.58(1:5)	23.49	31.07	2.48
Allyl	430	2.86(1:0.5)	18.64	21.50	1.17
Chloride		0.24(1:1)	47.51	47.75	1.12
		0.87(1:3)	17.94	18.81	1.11
1-Bromo-	400	1.30(1:0.5)	34.70	36.0u	3.03
3-Chloropropane		0.94(1:1.5)	17.21	18.15	2.98
		2.32(1:10)	15.18	17.50	3.02

*S:I = ratio of sample & inhibitor.

out, *i.e.*, pyrolysis of allyl bromide, allyl chloride and 1-bromo-3-chloropropane, respectively.

For 1-bromo-3-chloropropane decompositions, two cases of the reaction progress, with and without radical scavenger, have been investigated at 400 °C. As shown in Figure 1, it was found that the rate of decomposition with the radical scavenger is much smaller than that without the radical scavenger. In Table 1, it is shown that the amount of inhibitors has little effect on the rate constants for the decompositions of allyl chloride, allyl bromide, and 1-bromo-3-chloropropane. Thus it can be reasonably assumed that in the presence of a radical scavenger only molecular elimination process (HBr or HCl elimination) is important. Since the C-Cl or C-Br fission to give Cl or Br atoms is expected to have much higher activation energy, the disappearance of original compounds is reasonably assumed to occur via low energy HCl and/or HBr elimination step.

The dependence of each reactant concentration on reaction times for our samples are shown in Figure 2. Since the
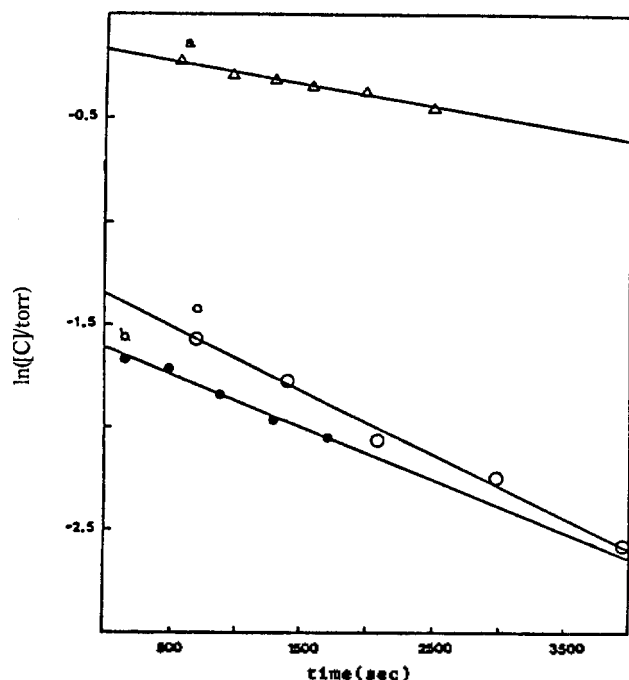
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Figure 2. Dependence of the reactant concentrations on reaction times. a: Allyl bromide Total Pressure 53.5 torr at 370 °C. b: Allyl chloride Total Pressure 7.06 torr at 430 °C. c: 1-Bromo-3-chloropropane Total Pressure 187.5 torr at 400 °C. [C]: Concentration.

Table 2. Average Rate Constants at Different Temperatures

Samples	Temp(°C)	No. of runs	$10^4 k (s^{-1})$	$10^5 \sigma_k (s^{-1})$
Allyl bromide	340	3	0.35	0.27
	350	3	0.85	0.60
	360	4	1.70	1.94
	370	9	2.58	0.67
	380	3	4.63	1.15
Allyl chloride	410	3	0.32	0.15
	420	3	0.62	0.25
	430	5	1.13	0.61
	440	3	1.96	0.75
	450	3	3.35	1.05
	460	4	4.23	1.52
1-Bromo-	380	3	0.99	0.09
3-chloropropane	390	4	2.26	0.50
	400	6	3.17	0.86
	410	4	5.50	2.26
	420	4	11.30	0.32

* σ_k: the standard deviation of k. * Total pressure in the system ca. 17 torr-100 torr.

In[reactant] *vs.* time plots gave straight lines in Figure 2 the reactions can be assumed to be 1st order, and the rate constants are obtained from the slope of the plots. The experimentally determined average rate constants of our samples at various temperatures are shown in Table 2. The Arrhenius parameters were obtained from the Arrhenius plots of these data as shown in Figure 3. The numerical data are shown in Table 3. For allyl bromide and allyl chloride the Arrhenius parameters were found to be; E_a's were 50.04, 52.78 (kcal/mol) and logA's were 13.41, 12.43 (sec^{-1}) respectively. For allyl chloride dissociation our experimentally de-
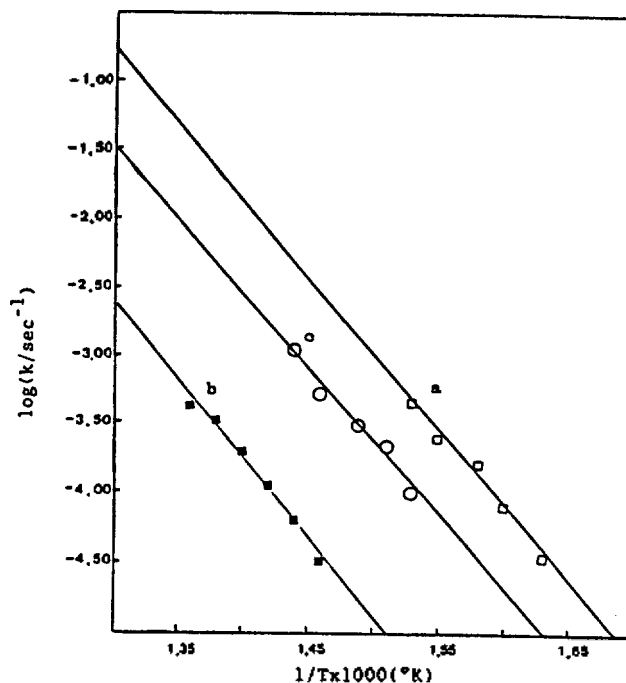

Figure 3. Arrhenius plots. a: allyl bromide. b: allyl chloride. c: 1-bromo-3-chloropropane.

Table 3. Experimentally, Determined Arrhenius Parameters for the Molecular Elimination Reactions

Samples	E_a(kcal/mol)	logA(sec^{-1})	r
Allyl bromide	50.04	13.41	0.9931
Allyl chloride	52.78	12.43	0.9942
1-Bromo-3-chloro-propane (overall)	51.83	13.36	0.9923
Dehydrobromination from $BrCH_2CH_2CH_2Cl$	49.75	12.54	0.9998
Dehydrochlorination from $BrCH_2CH_2CH_2Cl$	56.10	14.20	0.9995

* r: correlation coefficient of Arrhenius plots.

termined activation energy(52.78 kcal/mol) and logA (12.43 sec^{-1}) are larger than that of the Goodall's[15]values (46 kcal/mol for E_a and 10.1 sec^{-1} for logA).

Since the apparent rate constants for the dissociation of 1-bromo-3-chloropropane involves k_1 and k_2 the following consideration is necessary to obtain the Arrhenius parameters for k_1 and k_2 steps individually. The rate equations of each reaction path can be represented as following.

$$-d[BCP]/dt = k_1[BCP] + k_2[BCP]$$

$$-d[AB]/dt = k_3[AB] - k_1[BCP]$$

$$-d[AC]/dt = k_4[AC] - k_2[BCP]$$

$$-d[AL]/dt = -k_3[AB] - k_4[AC]$$

The final solutions of above equations are [16-19]:

$$[BCP] = [BCP]_o \exp(-(k_1+k_2)t) \tag{1}$$

$$[AB] = k_1[BCP]_o (\exp(-(k_1+k_2)t)$$
$$-\exp(-k_3 t))/(k_3-k_1-k_2) \tag{2}$$

$$[AC] = k_2[BCP]_o (\exp(-(k_1+k_2)t)$$
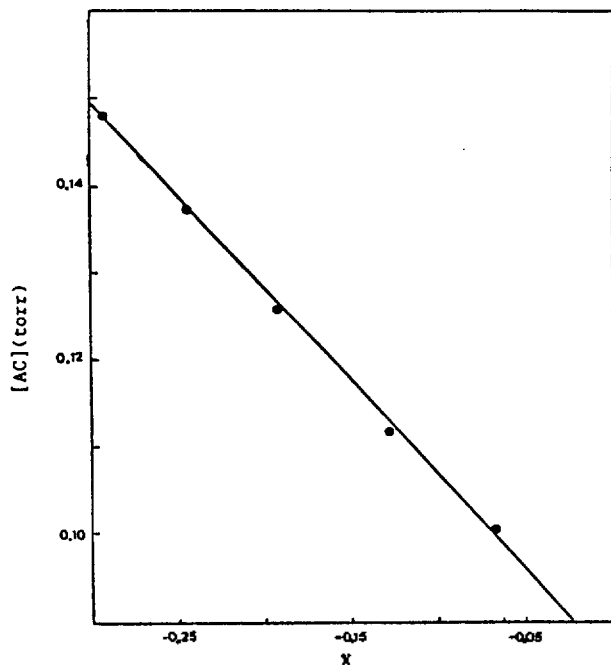$$-\exp(-k_4 t))/(k_4-k_1-k_2) \tag{3}$$

Figure 4. Least square plots to obtain k_2 at 380 °C. [AC]: concentration of allyl chloride. X: $\exp(-(k_1 + k_2)t) \cdot \exp((-k_4)t)$.
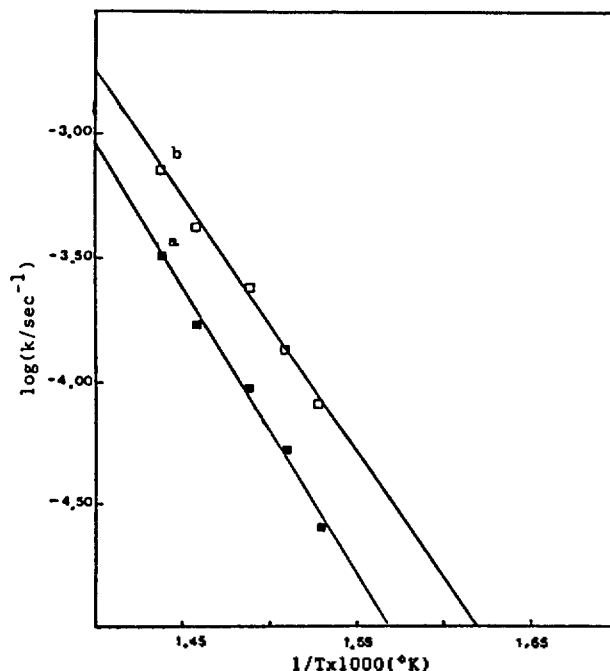
Table 4. The Rate Constants of Dehydrohalogenation from BrCH₂CH₂CH₂Cl at Different Temperature and Pressure

Temp(°C)	P(torr)	$10^4 k_1$(sec^{-1})	$10^4 k_2$(sec^{-1})
380	48.10	0.26	0.81
390	17.54	0.54	1.37
400	18.50	0.95	2.48
410	18.13	1.75	4.31
420	19.04	3.26	7.25

* k_1: dehydrochlorination of BrCH₂CH₂CH₂Cl. k_2: dehydrobromination of BrCH₂CH₂CH₂Cl.

$$[AL] = [BCP]_o - [BCP] - [AB] - [AC] \qquad (4)$$

where,   [BCP] = concentration of 1-bromo-3-chloropropane,

[AB] = concentration of allyl bromide,

[AC] = concentration of allyl chloride, and

[AL] = concentration of allene.

Equations (2) and (3) are useful for the determination of k_1 (dehydrochlorination rate constant of BrCH₂CH₂CH₂Cl) and k_2 (dehydrobromination rate constant of BrCH₂CH₂CH₂Cl). That is, k_1 or k_2 can be obtained from the slope of the least square plots of [C] against X (in this case, [C] = [AB] or [AC], $X = \exp(-(k_1 + k_2)t) - \exp((-k_{3,4})t)$ where, $k_{3,4} = k_3$ or k_4, t = reaction time). The $k_1 + k_2$ is the overall rate constant for the molecular dissociation of 1-bromo-3-chloropropane and k_4 is the rate constant for the allyl chloride decomposition. Therefore the rate constant, k_2, could be obtained by monitoring [AC] and reaction time. In Figure 4, the least square plot of [AC] versus X is shown at 380 °C. The results of k_1 and k_2 at various temperature are shown in Table 4. The Arrhenius plots of these data and the Arrhenius parameters are shown in Figure 5 and Table 3, respectively.

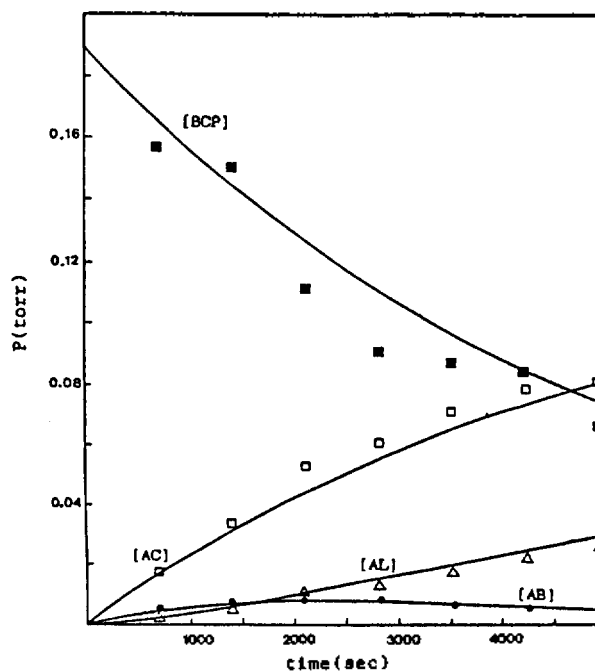The activation energy (49.75 kcal/mol) obtained for the

Figure 5. Arrhenius plots. a: dehydrochlorination from BrCH₂CH₂CH₂Cl. b: dehydrobromination from BrCH₂CH₂CH₂Cl.

Figure 6. Time dependence of reactant and product concentrations for the decomposition of BrCH₂CH₂CH₂Cl at 390 °C. — : calculated results.

dehydrobromination from 1-bromo-3-chloropropane is similar to that of 1-bromopropane (50.7-51.9 kcal/mol)[3-5], and that (56.10 kcal/mol) for the dehydrochlorination from 1-bromo-3-chloropropane is similar to that of 1-chloropropane (55.0 kcal/mol)[8].

Using the equations given above, the variation of the concentration of products and reactants with time can be simulated. The results at 390 and 410 °C are shown in Figure 6 and 7.
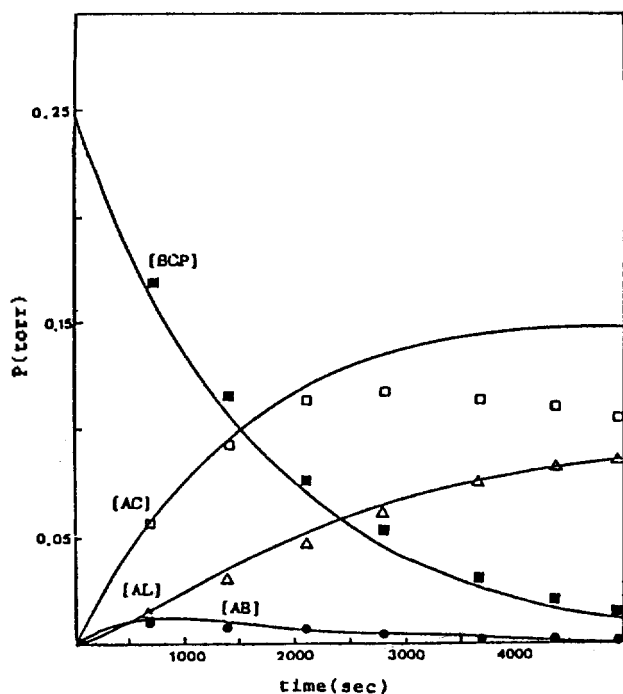
Figure 7. Time dependence of reactant and product concentrations for the decomposition of $BrCH_2CH_2CH_2Cl$ at 410 °C. —: calculated results.

(models of complex)

$CH_2=C\text{-}CH_2$ $H\text{-}Br$	$CH_2=C\text{-}CH_2$ $H\text{-}Cl$	$ClCH_2\text{-}CH\text{-}CH_2$ $H\text{-}Br$	$BrCH_2\text{-}CH\text{-}CH_2$ $H\text{-}Cl$
(a)			
6.24×10^6	2.88×10^6	1.78×10^8	1.68×10^8
$\nu(cm^{-1})$	$\nu(cm^{-1})$	$\nu(cm^{-1})$	$\nu(cm^{-1})$
3050 (2)	3050 (2)	3000 (5)	3000 (5)
2950 (2)	2950 (2)	1351 (5)	1351 (5)
1640	1640	1166 (3)	1166 (3)
1440 (2)	1440 (2)	946 (3)	946 (3)
1310	1310	762 (3)	762 (3)
1300 (2)	1300 (2)	600	520
990	1100	500	430
970	1000	460	250
910	990 (2)	380	130
850 (2)	930 (2)	240	110
580 (2)	910	150	100
440 (2)	890	88	(82)
223	830	(56)	52
(200)	580		
	(300)		

*(a): $I_{xyz}(g^3cm^6)$ in unit (10^{-120}).

Table 6. Pressure Dependence of the Rate Constants

Samples	Temp(°C)	P (torr)	$10^4 k$ (sec^{-1})
Ally bromide	370	3.99	2.49
		9.42	2.50
		17.44	2.53
		53.50	2.57
		95.00	2.67
		167.70	2.67
Allyl chloride	430	0.04	0.72
		0.08	0.78
		0.24	0.87
		0.51	1.15
		15.21	1.18
		88.23	1.19
1-Bromo-	400	0.21	2.78
3-chloropropane		0.90	2.95
		17.00	3.24
		88.00	3.30

To find out whether the rate constants given above have any pressure dependence, RRKM calculations were carried out. In Table 5, the input data for RRKM calculation are presented. Vibrational frequencies of allyl bromide molecule were obtained from the results of Tsang's report[20] and those of its complex were assumed to have the values which gave similar Arrhenius A factor to the experimental results. Similarly, those of allyl chloride and 1-bromo-3-chloropropane molecule were taken from the Tsang's report[20] and Setser's report[21] respectively and their complex frequencies were assumed according to the above method. In the calculation of the moments of inertia for activated complex,

Table 5. Input Parameters for RRKM Calculations (Models of molecule)

	C_3H_5Br	C_3H_5Cl	ClC_3H_6Br
	(a)		
$I_{xyz}(g^3cm^6)$	9.20×10^6	3.88×10^6	1.23×10^8
L^*	1	1	2
	$\nu(cm^{-1})$	$\nu(cm^{-1})$	$\nu(cm^{-1})$
	3050 (3)	3050 (3)	2951 (6)
	2950 (2)	2950 (2)	1451 (5)
	2640	1640	1216 (3)
	2440 (2)	1440 (2)	946 (3)
	1415	1415	762 (3)
	1370	1330 (2)	600
	1207	1200	500
	1172	1050	310
	1050	990	170
	990	920 (2)	110
	930	650	82
	911	600	56
	580 (2)	400 (2)	
	417	300	
	290		
	200		

collision diameter: $CH_2=CH\text{-}CH_2Br$ — Ar: 4.50 Å
$CH_2=CH\text{-}CH_2Cl$ — Ar: 4.43 Å
$BrCH_2CH_2CH_2Cl$ — Ar: 4.85 Å

*(a): in unit (10^{-120}). L^*: reaction path degeneracy.

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Table 7. Pressure Dependence of the Rate Constants by RRKM Calculations (Allyl bromide & Allyl chloride)

Samples	Temp(°C)	P(torr)	$10^4 k$ (sec⁻¹)			
			β: 1.00	0.75	0.50	0.25
Allyl bromide	370	0.01	0.45	0.39	0.32	0.23
		0.05	0.82	0.74	0.65	0.49
		3.99	1.70	1.67	1.62	1.52
		9.42	1.76	1.74	1.71	1.64
		17.44	1.79	1.78	1.75	1.71
		53.50	1.81	1.81	1.80	1.77
		95.00	1.82	1.82	1.81	1.78
		167.70	1.83	1.82	1.82	1.81
		500.00	1.83	1.83	1.83	1.82
		1000.00	1.83	1.83	1.83	1.83
Allyl chloride	430	0.01	1.04	0.95	0.83	0.63
		0.04	1.47	1.39	1.26	1.04
		0.08	1.66	1.59	1.47	1.26
		0.24	1.89	1.84	1.76	1.59
		0.51	2.00	1.97	1.90	1.77
		15.21	2.17	2.16	2.16	2.14
		88.23	2.17	2.17	2.17	2.17
		218.80	2.17	2.17	2.17	2.17
		1000.00	2.17	2.17	2.17	2.17

* β: collision efficiency.

(1-Bromo-3-chloropropane)

Samples	Temp(°C)	P(torr)	$10^4 k$ (sec⁻¹)			
			β: 1.00	0.75	0.50	0.25
-HCl from	400	0.01	0.38	0.36	0.32	0.25
BrCH₂CH₂CH₂Cl		0.03	0.49	0.47	0.42	0.36
		0.07	0.57	0.55	0.50	0.44
		0.10	0.60	0.58	0.51	0.44
		0.21	0.73	0.73	0.61	0.55
		0.90	0.77	0.73	0.70	0.66
		17.00	0.79	0.78	0.78	0.77
		88.00	0.79	0.79	0.79	0.79
		187.50	0.79	0.79	0.79	0.79
-HBr from	400	0.01	1.72	1.64	1.53	1.33
BrCH₂CH₂CH₂Cl		0.03	1.95	1.90	1.81	1.64
		0.07	2.08	2.05	1.98	1.85
		0.10	2.13	2.09	2.04	1.93
		0.21	2.19	2.17	2.13	2.05
		0.90	2.25	2.24	2.23	2.19
		17.00	2.28	2.28	2.28	2.27
		88.00	2.28	2.28	2.28	2.28
		187.50	2.28	2.28	2.28	2.28

* β : collision efficiency.

the bond order was assigned to be 1.8(C-C), 0.8(C-X), 0.2 (H-X), 0.2(H-C) for the calculation of bond length through Pauling's equation[22] and the bond angle (H-C-C, C-C-X)

was assigned to be 110° for allyl bromide and allyl chloride, and 100° for 1-bromo-3-chloropropane respectively.

The pressure dependence experiments were carried out in the range of 3.0-168, 0.04-89.0 and 0.21-88.0 torrs for allyl

Table 8. Comparison of Calculated and Experimental Fall-Off Curves (Allyl bromide & Allyl chloride)

Samples	Temp(°C)	log (P/torr)	Experiment	RRKM Calculation			
			$-\log (k_{uni}/k_\infty)$	$-\log (k_{uni}/k_\infty)$			
			β: 1.00	0.75	0.50	0.25
Allyl bromide	370	-2.00	—	0.611	0.667	0.751	0.908
		-1.30	—	0.350	0.390	0.452	0.570
		0.60	0.030	0.033	0.040	0.053	0.082
		0.97	0.029	0.017	0.021	0.029	0.047
		1.24	0.023	0.010	0.013	0.018	0.031
		1.73	0.017	0.004	0.005	0.007	0.013
		1.98	0.000	0.002	0.003	0.004	0.008
		2.22	0.000	0.001	0.002	0.002	0.005
		2.70	—	0.000	0.001	0.001	0.002
		3.00	—	0.000	0.000	0.000	0.001
Allyl chloride	430	-2.00	—	0.319	0.359	0.420	0.539
		-1.40	0.218	0.169	0.195	0.236	0.319
		-1.10	0.183	0.117	0.137	0.169	0.236
		-0.62	0.136	0.060	0.072	0.092	0.137
		-0.29	0.015	0.036	0.044	0.058	0.089
		1.18	0.004	0.002	0.003	0.004	0.007
		1.95	0.000	0.000	0.000	0.001	0.001
		2.34	—	0.000	0.000	0.000	0.001
		3.00	—	0.000	0.000	0.000	0.000

(1-Bromo-3-chloropropane)

| Samples	Temp (°C)	log (P/torr)	Experiment	RRKM Calculation			
			$-\log (k_{uni}/k_{\infty})$	$-\log (k_{uni}/k_{\infty})$			
			β : 1.00	0.75	0.50	0.25	
-HCl from BrCH$_2$CH$_2$CH$_2$Cl	400	-2.00	—	0.312	0.346	0.398	0.496
		-1.52	—	0.203	0.228	0.268	0.346
		-1.15	—	0.138	0.158	0.190	0.253
		-1.00	—	0.116	0.134	0.161	0.219
		-0.68	0.073	0.078	0.091	0.113	0.158
		-0.46	0.045	0.032	0.038	0.050	0.075
		1.23	0.005	0.003	0.004	0.005	0.010
		1.94	0.000	0.001	0.001	0.001	0.002
		2.27	—	0.000	0.000	0.001	0.001
-HBr from BrCH$_2$CH$_2$CH$_2$Cl	400	-2.00	—	0.123	0.142	0.173	0.234
		-1.52	—	0.067	0.079	0.099	0.142
		-1.15	—	0.039	0.047	0.061	0.091
		-1.00	—	0.031	0.037	0.049	0.075
		-0.68	0.073	0.018	0.022	0.030	0.047
		-0.46	0.045	0.005	0.007	0.010	0.017
		1.23	0.005	0.000	0.000	0.001	0.001
		1.94	0.000	0.000	0.000	0.000	0.000
		2.27	—	0.000	0.000	0.000	0.000

* β = collision efficiency.
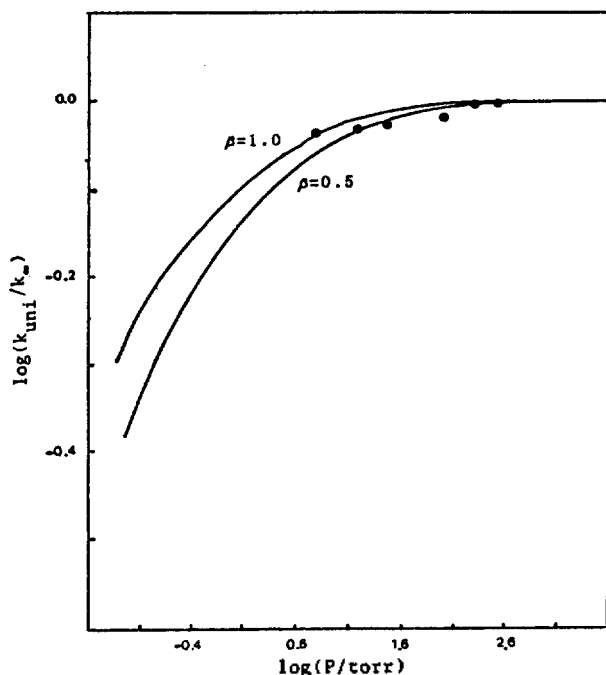
Figure 8. Comparison of calculated and experimental fall-off curves for allyl bromide decomposition at 370 °C. β: collision efficiency.

Figure 9. Comparison of calculated and experimental fall-off curves for allyl chloride decompositions at 430 °C. β: collision efficiency.

bromide, allyl chloride and 1-bromo-3-chloropropane, respectively. It is well known that the rate constants of small molecule with a few oscillators show a strong pressure dependence at moderate pressures. Thus it was predicted that the decomposition of allyl bromide and allyl chloride would show larger pressure dependence than that of 1-bromo-3-chloro-
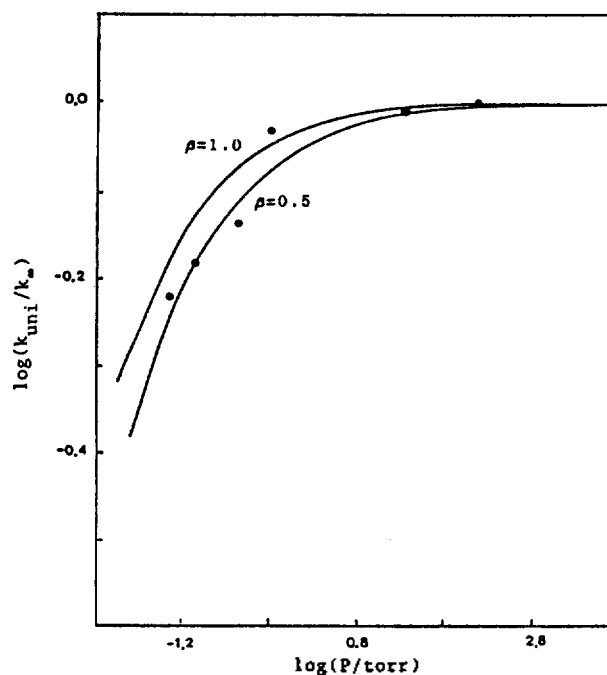
propane. The results of pressure dependence experiments of our samples are shown in Table 6.

To interpret the fall-off behavior of our samples, RRKM calculation was adopted and the pressure dependent rate constants were calculated at different collision efficiencies(β). The results are shown in Table 7. In Table 8
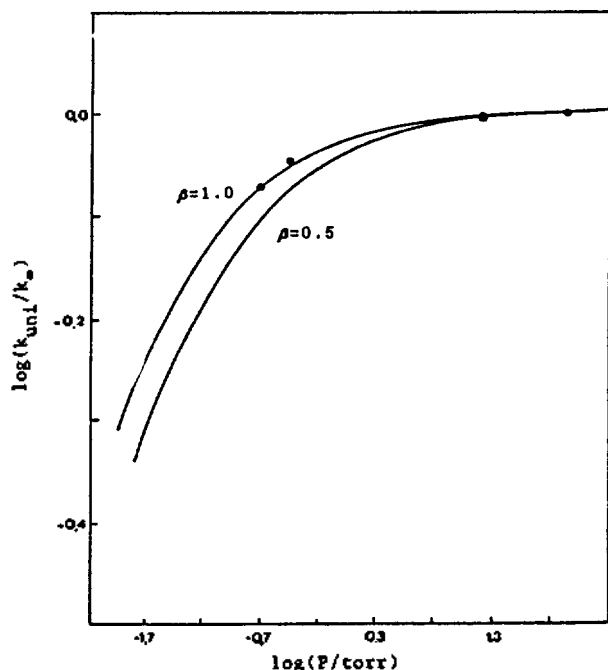
Thermal Decomposition of ClCH₂CH₂CH₂Br

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Figure 10. Comparison of calculated and experimental fall-off curves for dehydrochlorination from BrCH$_2$CH$_2$CH$_2$Cl at 400 °C. β: collision efficiency.
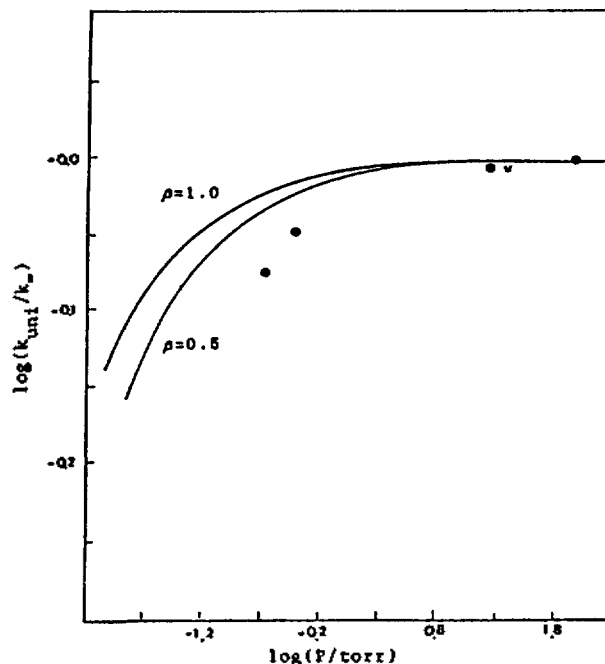
Figure 11. Comparison of calculated and experimental fall-off curves for dehydrobromination from BrCH$_2$CH$_2$CH$_2$Cl at 400 °C. β: collision efficiency.

and Figures 8-11 shows the comparison of RRKM calculated and experimental fall-off curves at different collision efficiencies.

From the pressure dependence studies and RRKM calculations, we can reasonably conclude that the Arrhenius parameters obtained in this work are the high pressure limiting values.

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