Kinetics of Thermal Gas-Phase Decomposition of 2-Bromopropene Using Static System

JAN NISAR, IFTIKHAR A. AWAN

National Center of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan

Received 26 April 2006; revised 26 June 2006; accepted 5 July 2006

DOI 10.1002/kin.20207 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The gas phase elimination kinetics of 2-bromopropene was studied over the temperature range of 571–654 K and pressure range of 12–46 Torr using the seasoned static reaction system. Propyne was the only olefinic product formed and accounted for >98% of the reaction. This product was formed by homogeneous, unimolecular pathways with high-pressure first-order rate constant k_{∞} given by the equation $k_{\infty} = 10^{13.47 \pm 0.6} \exp^{-208.2 \pm 6.7(k)} \mod^{-1})/\text{RT}$. The error limits are 95% certainty limits. The observed Arrhenius parameters are consistent with the four centered activated complex. The presence of methyl group on α -carbon lowers the activation energy by 41 kJ mol⁻¹. © 2006 Wiley Periodicals, Inc. Int J Chem Kinet 39: 1–5, 2007

INTRODUCTION

Although there have been numerous studies of the gas phase thermal dehydrohalogenation of alkyl halides and have been reviewed [1–3], there have been few examples in these studies of vinylic halides. The only experimental studies on hydrogen halide elimination from unsaturated compounds are those for HCl and HBr elimination from vinyl chloride [4,5] and vinyl bromide [6], and a recently reported study by Roy et al. [7] of the decomposition of 2-bromopropene and 2-chloropropene over a temperature range from 1100 to 1250 K using single pulse shock tube techniques.

The purpose of this paper is to present the kinetics of the thermal gas phase dehydrobromination reaction of 2-bromopropene at lower temperatures attainable under static system conditions using seasoned reactors. The study extends the range of temperature for the unimolecular decomposition of $2\text{-}C_3\text{H}_5\text{Br}$.

EXPERIMENTAL

Materials

2-Bromopropene (freezing point 4° C and boiling point $47-49^{\circ}$ C) was obtained commercially (Acros, 99+%) and tested for impurities by gas chromatography. Mesitylene (Acros) was used as a radical scavenger.

Kinetic Experiments

All thermal kinetic studies were carried out in a conventional "static" system using Pyrex reaction vessels [8]. Two reaction vessels were employed; one was packed with short lengths of Pyrex tubing to give a surface to volume ratio (S/V) of ca. 12 cm⁻¹, and the



Correspondence to: Iftikhar A. Awan; e-mail: iftikhar.awan@ nist.gov.

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other was of similar external dimensions but not packed $(S/V \text{ ca. } 1 \text{ cm}^{-1}, \text{ volume ca. } 150 \text{ cm}^3)$. Young's greaseless stopcocks were used in all parts of the vacuum system in contact with pyrolyzed material. The reactions vessels were kept at constant temperature in a salt bath constructed out of stainless steel can 30 cm in depth, 21 cm in diameter; this was logged and ternary eutectic enclosed in $42 \times 42 \times 44$ cm steel box. The salts used were sodium nitrite (7.1 mol), sodium nitrate (1 mol), and potassium nitrate (6.4 mol). The bath was heated by a heater that was made up of an 8-m length of stainless steel heating cable. The temperature of the bath was controlled by Rotatherm ADP 15 temperature controller. The reaction temperature was measured using the PT-100 platinum resistance thermometer with an accuracy of $\pm 0.1^{\circ}$ C. Reactions vessels were seasoned by pyrolysis of ca. 30 Torr 2-bromopropene at 500°C for 48 h. The reaction mixtures were analyzed by gas chromatography using Shimadzu GC 7AG gas chromatograph with a flame ionization detector. Analvses were carried out using stainless steel 6 ft \times 1/8 in. prepacked Porapak Q. Typical chromatographic conditions were column oven temperature = $70-170^{\circ}$ C, temperature-programming rate = 32° C min⁻¹, carrier gas = nitrogen, flow rate of carrier gas = 60 mL min^{-1} , hydrogen pressure = 1 kg cm⁻², air pressure = 0.5 kg cm^{-2} , and injection port temperature = 170°C. The areas under the peaks were determined using the Spectra Physics model SP-4600 data jet integrator. The identification of products was carried out by comparison of the retention times of authentic samples with those of unknown.

RESULTS AND DISCUSSION

Over the temperature range 571–654 K, 2bromopropene decomposed to give propyne as a reaction product. The rates of formation of this product mirrored the rate of disappearance of 2-bromopropene.

$$CH_3 - C(Br) = CH_2 \rightarrow CH_3 - C \equiv CH + HBr$$

First-order rate plots for the loss of 2-bromopropene using 20 Torr initial pressure were linear as shown in Fig. 1. The rate constants based on the loss of initial reactant were obtained at 11 temperatures and are listed in Table I. The Arrhenius dependence of the rate constants is given by

$$k_{\text{(total)}} = 10^{13.47 \pm 0.6} \exp^{-208.2 \pm 6.7 (\text{kJ mol}^{-1})/RT}$$

The plot is given in Fig. 2.

The effect of surface on the reaction was investigated at high, middle, and lower temperatures using



Figure 1 First-order rate plot for the loss of 2bromopropene at 611.5 K. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

the packed reaction vessel. Kinetic runs were carried out in both packed and unpacked reaction flasks with a pressure of 20 Torr and pyrolysis time of 15 min. It was observed that the contribution of surface is maximum at lower temperature and minimum at high temperature. The surface to volume ratio ranges from 0.22 to 0.63% in the temperature range (576.2–643.2 K) studied.

The effect of change in pressure on the reaction rate was studied at 611.5 K. The effect of pressure on the percent product is graphically represented in Fig. 3. It is shown that pressure has no effect on the rate of reaction, and the observed Arrhenius parameters are close to high pressure limit.

To reduce the amount of secondary radical reactions taking place in the system, mesitylene was added as a radical trap. In the presence of 10% mesitylene, the rate decreases only by 3.89%, which is within the experimental error.

The decomposition of 2-bromopropene to propyne is the result of first-order, homogeneous, nonradical, and unimolecular reaction. The observed activation parameters log A = 13.47 s⁻¹ and $E_a = 208.2$ kJ mol⁻¹

Table IRate Constant for 2-BromopropeneDecomposition at 20 Torr Initial Pressure

Temperature (K)	$k_{\text{(total)}} (\mathrm{s}^{-1})$	
570.9	2.30E-06	
576.4	4.80E-06	
583.4	9.6E-06	
593.7	1.15E-05	
603.4	3.07E-05	
611.5	3.84E-05	
621.2	8.96E-05	
633.3	2.03E-04	
643.1	4.99E-04	
649.2	5.34E-04	
654.2	6.58E-04	



Figure 2 Arrhenius plot for 2-bromopropene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

are consistent with semi-ionic four centered transition state for the elimination of HBr.

$$CH_2 = C - CH_3 \Longrightarrow \begin{array}{c} \beta \\ CH_2 = C \\ Br \end{array} \xrightarrow{\alpha_{+\delta}} CH_3 \longrightarrow CH = C - CH_3 + HBr \\ H \\ H \\ Br \end{array}$$

A comparison of the rate constants of 2-bromopropene with vinyl bromide at 600 K shows that the former reaction is four orders of magnitude faster (see Table II). Assuming similar transition state in both reactions, this increase in rate can be assigned entirely to the change in the activation



Figure 3 Pressure dependence study for the decomposition of 2-bromopropene at 611.5 K (reaction time 10 min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

energy. The observed reduction by 41 kJ mol⁻¹ for 2-bromopropene compared to vinyl bromide can be attributed to the stabilization of transition state due to the presence of methyl group at α -carbon atom. A similar trend has been observed for 2-bromopropane compared with bromoethane.

The first-order dissociation rate constants have been theoretically modeled with a distinct Rice, Ramsperger, Kassel, Marcus (RRKM) calculation using the Chemrate program. In Table III, the input data for RRKM calculation are presented. Vibrational frequencies of 2-C₃H₅Br molecule and those of its complex were obtained from the results of Lee and Kim report [12]. The calculations of the moment of inertia for the molecule and activated complex are also based on the same report. $\Delta_f H^\circ$ of 2-C₃H₅Br molecule was obtained from NIST Kinetics Database [13] and that

Reactant	$E_{\rm a}$ (kJ mol ⁻¹)	$\log A \ (\mathrm{s}^{-1})$	log <i>k</i> at 600 K	Reference	
C ₂ H ₃ Br	249.4	13.33	-8.38	[9]	
2-C ₃ H ₅ Br	208.2 ± 6.7	13.47 ± 0.6	-4.64	This work	
C ₂ H ₅ Br	225.5	13.3	-7.2	[10]	
2-C ₃ H ₇ Br	200	13.6	-3.67	[11]	

Table II High Pressure Arrhenius Parameters for Decomposition of Alkyl Bromide

 Table III
 Input Parameters used in RRKM Calculation for 2-Bromopropene Decomposition^a

	Species		
	CH ₃ —C(Br)=CH ₂	[CH ₃ -C(Br)=CH ₂] [#]	
$\Delta H_f 298 \text{ K } (\text{kJ mol}^{-1})$	69.9^{b}	270 ^c	
Moment of inertia $(10^{-19} \text{ kg m}^2)$	$I_x = 6.8145, I_y = 6.8145,$ $I_z = 6.8145$	$I_x^{\#} = 6.5693, I_y^{\#} = 6.5693, I_z^{\#} = 6.5693$	
Frequencies	3242, 3146, 3106, 3031, 1696, 1488, 1435, 1411, 1178, 1015, 928, 543, 354, 301, 3089, 1470, 1072, 926, 700, 429, 209	3258, 3144, 3137, 3013, 1512, 1477, 1384, 1351, 1205, 1006, 936, 606, 359, 324, 3057, 1433, 1024, 962, 444, 330	

^a After [12].

^b After [13].

^c Adjusted to get best fit.



Figure 4 Comparison of calculated and experimental rate constants for thermal decomposition of 2-bromopropene. Filled squares represent experimental results, and open squares denote calculated data. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

of its complex was assumed to have the value, which give similar Arrhenius A factor to the experimental results.

RRKM-treated data exactly reproduced the experimental rate constants over the entire temperature range studied. This is represented in Fig. 4. The agreement is fairly satisfactory. There is a very small difference in values of activation energy and pre-exponential factor. The activation energy and A factor in the case of experimental results are about 2.23% and 3.5%higher than the RRKM results, respectively. This very small difference in the Arrhenius parameters is probably within the combined experimental errors of all determinations.

To interpret the falloff behavior of our sample, RRKM calculations were adopted and the pressuredependent rate constants were calculated at collision efficiency of 0.4. The falloff behavior is represented in Fig. 5. On the basis of 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. Thus, minimal errors are introduced by the extrapolation procedure. Whatever, the uncertainty is due to the fact that no purely vibrator rotor transition state for bond breaking can fit experimental results over the entire temperature range for bond-breaking



Figure 5 Comparison of calculated and experimental falloff curves for 2-bromopropene at 611.5 K. Filled squares represent experimental results, and open squares represent calculated data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Figure 6 Arrhenius plot showing comparison of static, shock tube and RRKM-treated data for thermal decomposition of 2bromopropene. Triangles denote shock tube results; circles represent RRKM-treated data, and diamonds represent static system investigations.

Method	Temperature (K)	$E_{\rm a}$ (kJ mol ⁻¹)	$\log A \ (\mathrm{s}^{-1})$	r	Reference
Shock tube (at 100 Torr)	1078.4–1221	274.4	14.93	0.9977	[7] This work
RRKM	720-840	208.2 203.8	13.03	0.9932	This work This work

Table IVComparison of Arrhenius Parameters Determined by Various Methods for Thermal Decomposition of2-Bromopropene

r =Correlation coefficient.

reactions. Tsang, while comparing the experimental results with the calculated results for decomposition of $3-C_3H_5Br$, observed that a satisfactory A_{α} factor is not obtained unless the moment of inertia of the two-dimensional rotor is lowered from 9×10^{-39} g cm² to 0.54×10^{-39} g cm² [14]. For this, he followed the Benson's prescription of a "hindered rotor" transition state [15].

An exact fit can be made when we use a slightly lower value of β (collision efficiency) 0.2–0.6. In the present investigations, we use $\beta = 0.4$. The same conclusion has also been drawn by Tsang in his report on 3-C₃H₅Br decomposition.

A combined Arrhenius plot of the present static, shock tube (at 100 Torr) and RRKM-treated data (in the temperature range of 720–840 K) is represented in Fig. 6, showing a good agreement between static and RRKM-treated data, but no satisfactory agreement of shock tube investigations with static and RRKM-treated data is observed. A comparison of Arrhenius parameters determined by all the three methods is given in Table IV. It can be seen from the table that the Arrhenius parameters deduced from the static system and RRKM-treated data are in consonant with each other but deviate considerably from the shock tube determinations.

CONCLUSION

2-Bromopropene decomposes in the temperature range 570.9–654.2 K to give propyne and hydrogen bromide. The decomposition proceeds by a unimolecular mechanism. The decomposition obeys first-order kinetics, and the rate constant, which is independent of initial

pressure, can be represented by

$$k_{\text{(total)}} = 10^{13.47 \pm 0.6} \text{ exp}^{-208.2 \pm 6.7 (\text{kJ mol}^{-1})/RT}$$

The pressure dependence study and RRKM calculation indicate that the Arrhenius parameters obtained in this work are the high pressure limiting values. The RRKM-treated data exactly reproduce the experimental rate constants over the entire temperature and pressure range studied.

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